Universidade de Aveiro Departamento de Ambiente e Ordenamento

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The impact of biofuels for road traffic on air quality: a modelling approach

Modelação do impacto do uso de biocombustíveis nos transportes rodoviários na qualidade do ar

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica da Doutora Myriam Lopes, Professora Assistente do Departamento de Ambiente e Ordenamento da Universidade de Aveiro e sob co-orientação científica da Doutora Alexandra Monteiro, docente convidada do Departamento de Engenharia e Gestão Industrial e Pós-doc no Departamento de Ambiente e Ordenamento da mesma Universidade, e do Doutor Markus Amann, co-lider do "Greenhouse Gas Initiative" do International Institute for Applied Systems Analysis (IIASA).

Apoio Financeiro do FEDER através do Programa Operacional Fatores de Competitividade (COMPETE) e por Fundos Nacionais através da FCT do PTDC no âmbito dos Projetos BIOGAIR (PTDC/AAC-AMB/103866/2008) e CLICURB (EXCL/AAG-MAA/0383/2012).

Apoio financeiro da Fundação para a Ciência e Tecnologia (FCT) através do POPH-QREN, comparticipado pelo Fundo Social Europeu (FSE) e por fundos nacionais do MCTES pela Bolsa de Doutoramento com a referência SFRH / BD / 60370 / 2009.

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agradecimentos

Às minhas Amigas e orientadoras Myriam Lopes e Alexandra Monteiro, por todo o apoio e orientação para o meu desenvolvimento científico.

Ao Professor Carlos Borrego e Professora Ana Isabel Miranda pela disponibilidade, dedicação, espírito crítico e ensinamentos científicos.

Ao GEMAC, que há 6 anos me acolheu e me faz sentir numa casa cheia de irmãos. Por me aturarem e me ensinarem tanto! A todos eles, mas em especial à Helena Martins, Anabela Carvalho, Joana Ferreira, Jorge H. Amorim, Joana Valente, Elisa Sá, minha companheira nesta “estrada” e Sandra Rafael companheira no BIOGAIR.

Um agradecimento especial aos ex-gemaquianos Pedro Cascão e Cláudia Pimentel, pela amizade e desabafos, e à Ana Cristina Carvalho, não só pela amizade e desabafos mas também pelo seu incrível sentido crítico, sabedoria e encorajamento em seguir em frente.

To Hendrik Elbern, Achim Strunk, Elmar Friese and Lars Nieradzik for having teaching me to work with the EURAD-IM modelling system.

A special thank you to the whole team of the experimental studies, in particular to those that made this work successful: Prof. Luís Serrano, Luís Tarelho, Ole Nielsen, Nuno Pires and Pedro Cascão (again), and also to Prio Energy for providing biodiesel gallons.

À FCT, pelo seu patrocínio financeiro através da Bolsa de Doutoramento (SFRH / BD / 60370 / 2009) e dos Projectos BIOGAIR (PTDC/AAC-AMB/103866/2008), o alicerce deste trabalho, e CLICURB (EXCL/AAG-MAA/0383/2012).

À Agência Portuguesa do Ambiente (APA), pelo financiamento de protocolos que tanto me ajudaram a ganhar experiência em modelação da qualidade do ar.

Aos meus pais, irmãos, sobrinhos, cunhados e tios, que mesmo longe, pelo apoio incondicional, paciência e incentivo na superação dos obstáculos.

palavras-chave

Biocombustíveis, transportes rodoviários, emissões de poluentes atmosféricos, qualidade do ar, modelação numérica, estratégia energética

resumo

A escolha de fontes energéticas para o sector dos transportes é uma das preocupações da sociedade moderna devido a questões relacionadas com o paradigma energético, e ao facto de este ser uma das principais fontes de polução do ar nas cidades, afectando significativamente a saúde humana e a sua qualidade de vida. Devido às limitações técnicas com que as formas de mobilidade avançadas ainda se deparam, os biocombustíveis são considerados uma alternativa viável para as próximas décadas, contribuindo para a redução de gases com efeito de estufa e estimulando o desenvolvimento rural.

Portugal, motivado pelas políticas Europeias, tem aposto nos biocombustíveis, em especial no biodiesel, a fim de atingir a meta da Directiva 2009/28/CE. No entanto, não são conhecidos os impactos na qualidade do ar decorrentes da utilização de biodiesel. Assim, este trabalho pretende clarificar esta situação respondendo à seguinte questão: a utilização de biodiesel promove uma melhoria na qualidade do ar em Portugal, particularmente nas áreas urbanas?

A primeira tarefa deste trabalho consistiu na caracterização da cadeia de biocombustíveis em Portugal, verificando-se que a cadeia tem problemas de sustentabilidade, uma vez que toda a matéria-prima usada é importada, não estando a promover a redução da dependência energética externa.

Posteriormente foram avaliados os impactos associados à utilização de biodiesel nas emissões de poluentes atmosféricos e na qualidade do ar em Portugal e em particular na área urbana do Porto, através da utilização do sistema de modelação numérica à mesoscala WRF-EURAD e tendo por base 2 cenários de emissões: o cenário de referência que considera que não é usado biodiesel e o cenário B20 que reflecte a utilização de um combustível constituído por 80% de gasóleo fóssil e 20% de biodiesel. Com este trabalho, verificou-se que o uso de B20 pode ajudar a controlar os níveis de poluição atmosférica tanto em Portugal como na área urbana do Porto, promovendo a redução das emissões de PM10, PM2.5, CO e COVNM e respectivas concentrações no ambiente atmosférico. Por outro lado, são esperados aumentos nas emissões de formaldeído, acetaldeído e acroleína com o uso de B20 e aumentos nas concentrações de NO_2 na área urbana do Porto. Apesar destes compostos serem considerados tóxicos e cancerígenos, os COVNM dominantes no gasóleo de origem fóssil, presentes em quantidades reduzidas no biodiesel, têm coeficientes de perigo crónico mais elevados. Assim, a utilização de B20 nos transportes rodoviários apresenta maiores benefícios para a saúde humana e para a qualidade do ar quando comparado com a utilização de gasóleo convencional.

keywords

Biofuels, road traffic, atmospheric pollutant emissions, air quality, numeric modelling, energy strategy

abstract

The selection of the energy source to power the transport sector is one of the main current concerns, not only relative with the energy paradigm but also due to the strong influence of road traffic in urban areas, which highly affects human exposure to air pollutants and human health and quality of life. Due to current important technical limitations of advanced energy sources for transportation purposes, biofuels are seen as an alternative way to power the world's motor vehicles in a near-future, helping to reduce GHG emissions while at the same time stimulating rural development.

Motivated by European strategies, Portugal, has been betting on biofuels to meet the Directive 2009/28/CE goals for road transports using biofuels, especially biodiesel, even though, there is unawareness regarding its impacts on air quality. In this sense, this work intends to clarify this issue by trying to answer the following question: can biodiesel use contribute to a better air quality over Portugal, particularly over urban areas?

The first step of this work consisted on the characterization of the national biodiesel supply chain, which allows verifying that the biodiesel chain has problems of sustainability as it depends on raw materials importation, therefore not contributing to reduce the external energy dependence.

Next, atmospheric pollutant emissions and air quality impacts associated to the biodiesel use on road transports were assessed, over Portugal and in particular over the Porto urban area, making use of the WRF-EURAD mesoscale numerical modelling system. For that, two emission scenarios were defined: a reference situation without biodiesel use and a scenario reflecting the use of a B20 fuel. Through the comparison of both scenarios, it was verified that the use of B20 fuels helps in controlling air pollution, promoting reductions on PM10, PM2.5, CO and total NMVOC concentrations. It was also verified that NO_2 concentrations decrease over the mainland Portugal, but increase in the Porto urban area, as well as formaldehyde, acetaldehyde and acrolein emissions in the both case studies. However, the use of pure diesel is more injurious for human health due to its dominant VOC which have higher chronic hazard quotients and hazard indices when compared to B20.

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Abbreviations

ACAP	Associação Automóvel de Portugal
AEBIOM	European Biomass Association
ANB	Average normalized absolute bias
APA	Agência Portuguesa do Ambiente
APC	Analytical Predictor of Condensation
APPB	Associação Portuguesa de Produtores de Biocombustiveis
B20	B20 Scenario / blend fuel with 20% (v/v) of biodiesel
Bias	Mean Systematic error
BIOFRAC	BIOfuel Research Advisory Council
BTX	Benzene, Toluene and Xylene
Bx	Blend fuel with x% (v/v) of biodiesel
CAM	Common ARTEMIS Motorway
CAU	Common ARTEMIS Urban
CAR	Common ARTEMIS Rural
C125	Simulation domain over the Europe and Northern Africa (125 $\times$ 125 km^2)
CADC	Common Artemis Driving Cycle
CAP	Common Agricultural Policy
CC	Carbonyl compounds
CCE	Carbonyl Compound Emission
CMQA	Community Multiscale Air Quality
DGEG	Direcção Geral de Energia e Geologia
DL	Decree-Law
EBB	European Biodiesel Board
EC	Elemental Carbon
EC	European Commission
ECU	Engine control unit
EEA	European Environment Agency
EEM	EURAD Emission Model
EF	Emission Factors
EGR	Exhaust Gas Recirculation
EIA	U.S. Energy Information Administration
EMEP	European Monitoring and Evaluation Programme
ENE2020	National Strategy to Energy 2020

Abbreviations

EOP	Equivalent Ozone Production
EU	European Union
EUDC	Extra-Urban Driving Cycle
EURAD-CTM	EURopean Air pollution Dispersion - Chemistry Transport Model
FAC2	Fact of two Observations
FAIRMODE	Forum for AIR quality MODelling in Europe
FAME	Fatty acid methyl ester
FB	Fractional bias
GFS	Global Forecast System
GHG	Greenhouse Gas
HDMR	High Dimensional Model Representation technique
HDV	Heavy duty vehicles
HPV	Heavy passenger vehicles
IA	Index of agreement
IEA	International Energy Agency
ILUC	Indirect land use change
INERPA	National Emission Inventory
IP25	Simulation domain over the Iberian Peninsula (25×25 km^2)
IPCC	Intergovernmental Panel on Climate Change
IPMA	Instituto Português do Mar e da Atmosfera
KF	Kalman filter
LCA	Life Cycle Assessment
LDV	Light duty vehicles
LNEG	Portuguese Laboratory for Energy and Geology
LPG	Liquid petroleum gas
LPV	Light passenger vehicles
MADE	Modal Aerosol Dynamics model for Europe
MEID	Ministério da Economia, Inovação e Desenvolvimento
MG	Geometric mean bias
MIM	Mainz Isoprene Mechanism
MIR	Maximum Incremental Reactivity
MMM	Mesoscale and Microscale Mateorology Division
MOBI.E	National Electric Mobility Network
NCAR	National Center for Atmospheric Research's
NCEP	National Centers for Environmental Prediction
NEDC	New European Driving Cycle
NMSE	Normalized mean squared error
NMVOC	Non-methane Volatile Organic Compounds
NOOA	National Oceanic and Armospheric Administration's

Abbreviations

NRL	Naval Research Laboratory
NSD	Normalized standard deviation
OBS	Observed values
OC	Organic Carbon
OP01	Simulation domain over the Porto urban area (1×1 km^2)
PAH	Aromatic Polyaromatic Hydrocarbons
PM	Particulate matter
PM10	Particulate matter with an aerodynamic diameter smaller than 10 μm
PM2.5	Particulate matter with an aerodynamic diameter smaller than 2.5 μm
PNAEE	National Action Plane for Energy Efficiency
PNAER	National Action Plane for Renewable Energies
ppbv	Parts per billion in volume basis
PPC	Pre-processor
PT05	Simulation domain over mainland Portugal (5×5 km^2)
R	Correlation coefficient
RACM-MIM	Regional Atmospheric Chemical Mechanism-Mainz Isoprene Mechanism
RAT	Multiplicative ratio correction
RAT04	Multiplicative ratio correction with 4 days training period
REDirective	Renewable Energy Directive
REF	Reference Scenario
RES	Renewable Energy Sources
RME	Root mean squared error
SD	Standard deviation
SNAP	Standardized Nomenclature for Air Pollutants
SOA	Secondary Organic Aerosols
SOF	Soluble Organic Fraction
SORGAM	Secondary ORGanic Aerosol Module
SUBST	Subtractive/additive correction of the mean bias
TREM-HAP	Transport Emission Model for line sources - Hazardous Air Pollutant
UDC	Urban Driving Cycle
UK	United Kingdom
USA	United States of America
VG	Geometric variance
VOC	Volatile Organic Compounds
WHO	World Health Organization
WPS	WRF Pre-processing System
WRF	Weather Research & Forecasting model
3D	Tridimensional

Symbols of elements and chemical compounds

$C_{16}H_{34}$	Hexadecane
$C_{19}H_{36}O_2$	elaidic acid methyl ester
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H_2O	Water
H_2O_2	Hydrogen peroxide
HC	Hydrocarbon
HCL	Hydrogen chloride
HF	Hydrogen fluoride
HNO_3	Nitric Acid
N_2	Nitrogen
N_2O_5	Dinitrogen pentoxide
NH_3	Ammonia
NH_4^+	amonium ion
NO	Nitric Oxide
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NOx	Nitrogen Oxides
O_2	Oxygen
O_3	Ozone
SO_2	Sulphur dioxide
SO_3^{2-}	Sulfite anion
SO_4^{2-}	sulphate ion
SOx	Sulphur Oxides
VOC	Volatile Organic Compounds

Chapter 1. Scope and structure of the work

The energy sector is a key factor in the socio-economic and environmental domains. The increasing industrialization and motorization of the world has led to a steep rise for the demand of fossil fuels. To fulfil the energy demand the sources of these fossil fuels are becoming exhausted. Today fossil fuels take up 80% of the primary energy consumed in the world, of which 20% is used in the transport sector (IEA, 2013). Furthermore, they are major contributors to greenhouse gas (GHG) emissions, which leads to adverse effects on climate change, receding of glaciers, rising sea level, increasing of extremes weather events and loss of biodiversity (IPCC, 2007). Progressive depletion of conventional fossil fuels with increasing energy consumption and GHG emissions have led to a move towards alternative, renewable, sustainable, efficient and cost-effective energy sources with less emissions (Zhao et al., 2009; He et al., 2010; Singh et al., 2010a, 2010b). Biomass[1] as an alternative energy source has taken an important rode in the worldwide energy strategy due to its multiple energy applications such as electricity, heat production and the use on transportation (biofuels). In fact, biofuels are seen as an alternative way to power the world's motor vehicles in a near-future, due to current important technical limitations of advanced energy sources for transports (e.g. electric and hydrogen fuel cell vehicles) (Felipe et al., 2014; URL 1 and URL 2). Additionally, they can help reducing GHG emissions and diversifying the energy sources from the transport sector, as well as stimulating rural development and creating jobs.

Biofuels have attracted great attention all over the world due to their renewability and availability, promising to contribute to regional and rural development as well as to improve environmental quality. However, there has been widespread debate in popular media and scientific journals about the sustainability of biofuels production and use,

[1] According to the Directive 2009/28/EC on the promotion of the use of energy from renewable sources, biomass is the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. Thus, biomass is biological material containing energy from recent carbon fixed.

related to social, economic, environmental and technical issues. The "food *vs* fuel" debate, the impacts of land use changes linked to deforestation and soil erosion, loss of biodiversity and impact on water resources, as well as the possible modifications on engine to be fuelled by biofuels, are examples of issues that led to several scientific studies and stimulated the definition of sustainability criteria. Actually, depending on feedstock and production technique, there are several biofuels and not all of them have similar performance in terms of their impact on climate, energy security and ecosystems. Thus, these impacts should be assessed, specifically for each biofuel and scenario, throughout the entire life cycle (Bringezu et al., 2009), helping different countries to adopt specific measures on biofuels introduction, including sustainability criteria (Nigam and Singh, 2011; Savaliya et al., 2013). Some sustainability criteria on biofuels are already included in the current European Directive 2009/28/EC on the promotion of the use of energy from renewable sources (Renewable Energy Directive, REDirective). Motivated by European strategies, Portugal has been betting on biofuels, particularly biodiesel, because diesel was, and still is, the main fuel consumed, representing about 75% (e/e) of the energy consumed by the national transport sector (URL 3). Thus, Portugal intends to meet the REDirective goals for road transports (replacement of 10% fossil fuels by renewable energy in the transportation sector by 2020) using biofuels, especially biodiesel. In fact, how to fuel the transport sector is one of the main concerns of modern society due to energy issues but also due to the strong influence of road traffic in urban areas, which highly affects human exposure to air pollutants and consequently human health and quality of life. According to the World Health Organization news release (WHO, 2014), 7 million premature deaths annually are linked to air pollution. Nevertheless there is a lack of knowledge with respect to the impacts of biodiesel blends use on regional and urban air quality.

In this sense, this work aims to assess the impact on air quality derived from the biodiesel blends usage on road transports by trying to answer this question: can biodiesel use contribute to a better air quality over Portugal, particularly over urban areas? Several experimental studies have demonstrated the benefits of diesel/biodiesel blends use on vehicles exhaust gases emissions, helping in controlling air pollution (Lapuerta et al., 2008; Xue et al., 2011). Moreover, road traffic is one of the main air pollution sources in European cities (EEA, 2013), largely contributing to high levels of nitrogen oxides (NOx), particulate matter with an aerodynamic diameter smaller than 10 μm (PM10) and 2.5 μm (PM2.5) measured at traffic monitoring stations (EEA, 2013).

To reach the goal of this work, the impacts on air quality over mainland Portugal and the Porto urban area were assessed making use of numerical modelling tools. This type of tools has become as fundamental to support decision makers on air quality management due to its ability to estimate atmospheric pollutants concentrations over the entire region of interest, taking into account complex and non-linear physic and chemical mechanisms that characterize the atmosphere, as well as to evaluate the efficiency of emission scenarios (Ribeiro et al., 2014). In this scope, the air quality numerical simulations were forced by CO, NOx, NH_3, sulfur oxides (SOx), PM10, PM2.5 and non-methane volatile organic compounds (NMVOC) emissions of all activity sectors. For the road transport sector, emission scenarios were designed considering that vehicles are powered by fossil fuels or by biodiesel blends.

Figure 1.1 presents the methodology defined to achieve the purposes of this work.

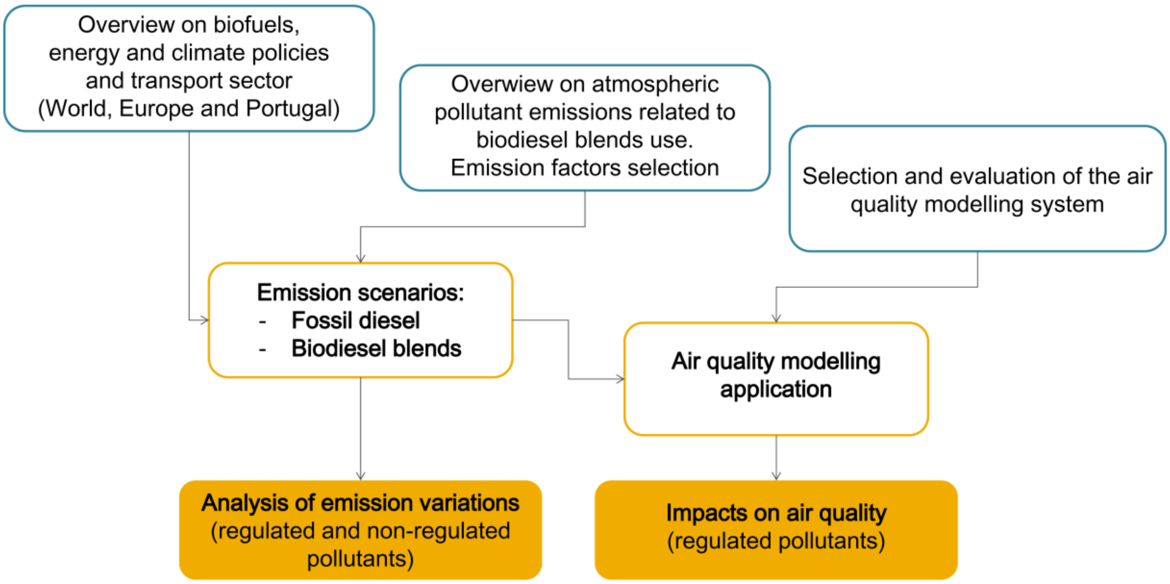


Figure 1.1 – Scheme of the defined methodology.

Firstly, an overview regarding the biofuels situation in the world and over Portugal was conducted and it is presented in Chapter 2. This chapter also includes the analysis of the Portuguese energy sector and the operation mode characterization of the national biodiesel supply chain. This characterization was carried out through a vast collection of information and statistical data from literature and contacts with stakeholders.

In parallel, a literature review regarding the effects on atmospheric pollutant emissions when diesel/biodiesel blends are used in diesel vehicles was accomplished (Chapter 3) aiming to define emission scenarios. Here, two main groups of atmospheric pollutants were analysed: the first group comprehends the regulated pollutants, such as CO, CO_2, NOx and NMVOC; and the second group includes the non-regulated pollutants, namely formaldehyde (CH_2O), acetaldehyde (C_2H_4O), benzene (C_6H_6) and acrolein (C_3H_4O). The interest on these non-regulated pollutants is related to their potential for tropospheric ozone formation, as well as their carcinogenic and toxic characteristics, which is especially important on urban areas due to human exposure to these pollutants.

Based on the emission factors from the use of diesel/biodiesel blends, two emission scenarios were defined for mainland Portugal and for the Porto urban area in Chapter 4. Regulated and non-regulated emissions were estimated regarding each scenario and case study, through the Transport Emission Model for line sources with Hazardous Air Pollutant (TREM-HAP, Tchepel et al., 2012). The analysis and comparison of both emission scenarios are also addressed in this chapter.

Chapter 5 is dedicated to the selection and description of the air quality numerical modelling system used to simulate both emission scenarios and to investigate the impacts of biodiesel blends use on road transports. In this sense, the air quality numerical modelling comprising the Weather Research & Forecasting (WRF, Skamarock et al., 2008) and the EURopean Air pollution Dispersion – Chemistry Transport Model (EURAD-CTM, Hass, 1991; Ebel et al., 1997; Elbern et al., 2007) was selected through a multi-model comparison exercise. A detailed description of the modelling system is given in this chapter, including the model setup defined for this study (simulation domains, physic and chemical parameterization options).

The performance of the WRF-EURAD modelling system is evaluated for both case studies (mainland Portugal and the Porto urban area), in Chapter 6, using observational and modelling data.

The emission scenarios developed in Chapter 4 were used as input data to the EURAD model to investigate the impacts of biodiesel blends use on air quality over both case studies, regarding CO, NO_2, NMVOC, O_3, PM10 and PM2.5 levels (Chapter 7).

Finally, in Chapter 8, a brief summary of the main results is carried out and the final conclusions are explored. Additionally, possible future developments are discussed.

Chapter 2. Biofuels in the World's and Portuguese contexts

This chapter gives a general overview of the biofuels world's history and production over the last decades. The European strategies on biofuels are also described and analyzed, as well as biofuels production in Europe. Aiming for a better understanding of the Portuguese situation on biofuels, the national energy sector is analyzed from the point of view of the road transport sector. Finally, the Portuguese biodiesel supply chain is characterized. It includes an overview of its operation as well as the biodiesel production from 2006 to 2012.

2.1 Biofuels in the World

By 1880s, Rudolph Diesel, who invented diesel engine, envisioned that vegetable oils could power diesel engines for agriculture in remote areas of the world, where petroleum was not available at that time. However, due to the low cost of the fossil fuels at that time, vegetable oils as an energy source were side-lined for decades. During petroleum crisis, in the 1970s, the world realized the pressing need to find alternative energy sources. Then renewable energy technologies were developed (Regnier, 2007; de Alegría Mancisidor et al., 2009). The first biofuel produced in an industrial scale was bioethanol in Brazil (1975) (Rosillo-Calle and Cortez, 1998), followed by biodiesel in Germany in 1991, according to the European Biodiesel Board website (URL 4).

Biofuels are renewable energy sources derived from biomass, which might replace petroleum fuels. Currently, the biofuels largely produced and consumed worldwide are bioethanol and biodiesel that can substitute gasoline and diesel, respectively. They can be produced through chemical conversion (acid hydrolysis, transesterification/esterification, supercritic fluid extraction, aqueous phase reforming), biological conversion (fermentation, anaerobic digestion, enzymatic hydrolysis, photochemical conversion) or by thermochemical conversion (combustion, gasification, pyrolysis, liquefaction) (Demirbas, 2009; Gupta and Demirbas, 2010). Biofuels can also be classified as traditional (or first generation biofuels) which are derived from food crops, while advanced biofuels (including second and third generations) are produced by non-food biomass, such as microalgaes (third generation biodiesels), cereal straw, forest residues, as well as industrial and domestic waste. Traditional biofuels are already in the market, but second and third generation biofuels are produced by advanced technologies, still under development, aiming at massive production (Demirbas, 2009; Gupta and Demirbas, 2010; Nigam and Singh, 2011).

Bioethanol fuels, widely used in the United States of America and in Brazil, are alcohols produced from sugar and starch crops, such as corn, sugarcane and sweet sorghum, but also from cellulosic biomass derived from non-food sources, namely forest biomass residues. This type of fuel can be used in its pure form, but it is usually used as a gasoline additive or substitute, replacing gasoline up to 85% (v/v), and contributing to improve vehicle performance and exhaust gases emissions (Jacobson, 2007; Demirbas, 2009; Gupta and Demirbas, 2010; Randazzo and Sodré, 2011). On the other hand, biodiesels are derived from vegetable oils (e.g. soybean, sunflower, palm oil, rapeseed, jathropha and microalgaes) or animal fats. They are commonly produced by converting vegetable oils into compounds called fatty acid methyl esters (FAME), throughout a transesterification reaction with methanol (Demirbas, 2007). This is the most common biofuel produced and used in European countries as an additive of petroleum-based diesel (URL 4), helping on reduction of particulate matter (PM), carbon monoxide (CO), and hydrocarbons (HC) emissions from diesel-powered vehicles (Lapuerta et al., 2008; Demirbas, 2009; Gupta and Demirbas, 2010; Xue et al., 2011).

Over the last decades, the European Union (EU) has adopted strategies (e.g. the Kyoto Protocol in 1997, and the European Climate Change Programme in 2001) to raise the diversification of energy sources, facing the external energy dependence, and the use of endogenous energy resources, contributing at the same time to reduce the GHG emissions and to encourage a more sustainable development. Thenceforth, the world's biofuel production has been growing. According to the U.S. Energy Information Administration (EIA, URL 5), from 2000 to 2011 the bioethanol output increased 5 times and the biodiesel output increased 26 times (Figure 2.1). This rapid growth in biofuels output is mostly supported by government policies which are driven by external energy dependence and energy security issues, coupled with the objective of revitalizing the agricultural sector and reducing GHG emissions from the transport sector.

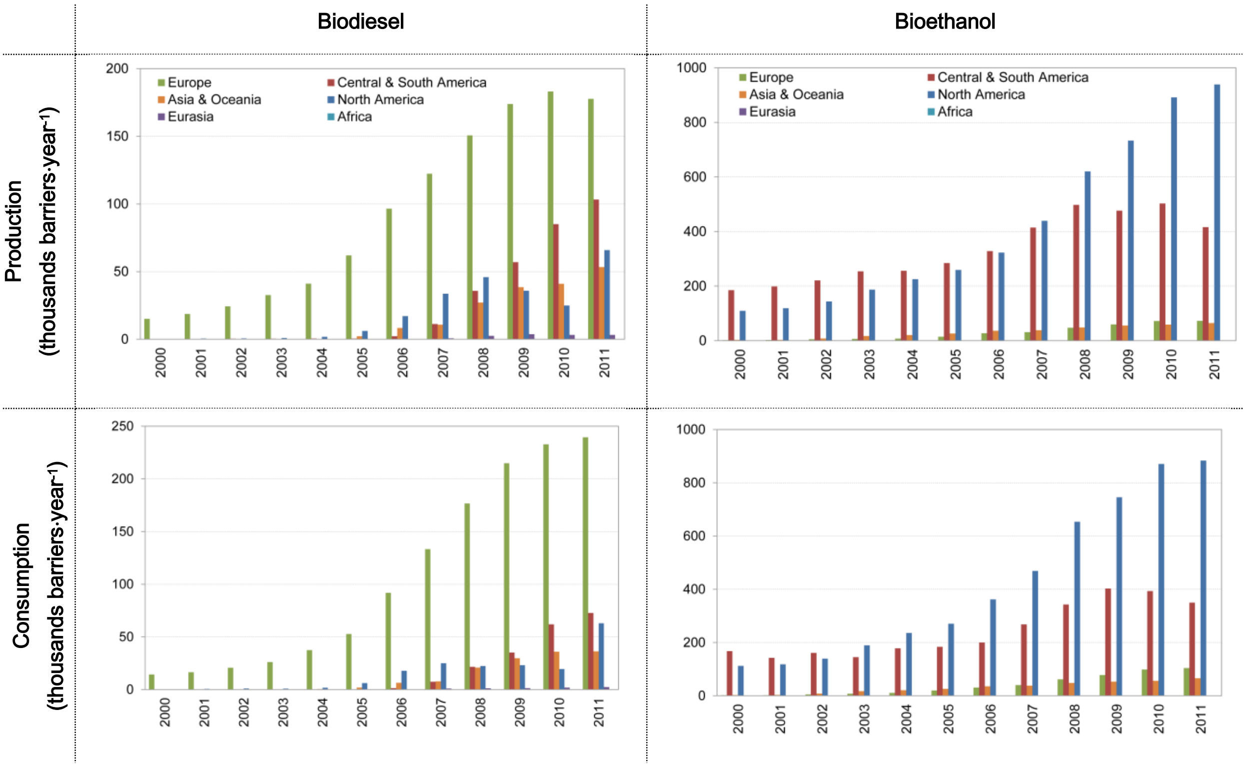


Figure 2.1 - Bioethanol/biodiesel production/consumption in the world from 2000 to 2011 (URL 5).

Bioethanol and biodiesel represent 84% and 16% of the biofuels production worldwide, respectively. Bioethanol is produced and consumed essentially in the USA and Brazil, from corn and sugar cane, while 60% of the biodiesel is produced by European countries, mostly Germany and France, from food feedstocks namely soybean, rapeseed and palm oil. The Europe is responsible for the consumption of 70% of biodiesel, which means that 10% of the European needs are imported from non-European countries (Figure 2.1). this difference between American and European countries are related to the importance of gasoline and diesel to fuel transport sector, respectively.

2.2 Biofuels in the Europe

Aiming to reduce GHG emissions and develop medium- to long-term alternatives for fossil fuels, reducing the external energy dependence, the EU launched the first Directive (2003/30/EC) on the promotion of the use of biofuels or other renewable fuels for transport. Three years later the "EU Strategy for Biofuels" (COM(2006) 34 final) was published, as a complement to the Biomass Action Plan from 2005. In its strategy, the European Commission defines the role that biofuels may play in the future as a renewable energy source (RES) and proposes measures to promote the production and use of biofuels in the EU countries. Seven strategic policy axes were set to:

1. **Stimulate demand for biofuels**, including the implementation and revision of the Directive 2003/30/EC;
2. **Capture environmental benefits** by highlighting the advantages of biofuels in terms of reducing emissions of GHG and guaranteeing that feedstock for biofuels is produced in a sustainable manner;
3. **Develop the production and distribution of biofuels**, highlighting the opportunities offered by biofuels in terms of economic activity and job creation within the context of the cohesion policy and rural development policy;
4. **Expand feedstock supplies** as a way to ensure sustainable production of biofuels;
5. **Enhance trade opportunities of biofuels**, including the insurance that European production and imports of biofuels are sustainable;
6. **Support developing countries** with potential in terms of biofuels, establishing a framework for effective cooperation including the development of national biofuel platforms and regional biofuel action plans;
7. **Support research and innovation** particularly in order to improve production processes and to lower costs, as well as by establishing a shared European vision and strategy for the production and use of biofuels.

Also in 2006, in an effort to implement future research and development of biofuels in Europe, a foresight report – "A vision for biofuels up to 2030 and beyond" was developed by a group of experts (BIOFRAC, 2006) invited by the European Commission. In this report the biofuels feedstocks, production and conversion techniques in Europe were evaluated and conclusions point out that by 2030 up to one quarter of the European's transport fuel needs could be met by clean and efficient biofuels. The BIOfuel Research Advisory Council (BIOFRAC) made fourteen recommendations, such as the needs on investigation and investments concerning advanced biofuels production and development of quality and environmental standards for biofuels.

In December 2008, the Climate and Energy Package (*aka* 20-20-20 targets) was adopted in order to reduce GHG emissions by 20% compared to 1990, to reduce the energy consumption by 20% through increased efficiency, and to achieve a 20% share of RES in gross final energy consumption until 2020. Under the 20-20-20 targets, the REDirective (2009/28/EC) establishes a common framework for the use of RES in order to limit GHG emissions and to promote cleaner transport, proposing sustainability criteria schemes for biofuels. These criteria include GHG emissions reductions, land use and environmental issues, as well as economic and social criteria, and adherence to the International Labour Organization conventions. These criteria are not only applicable to the biofuel supply chain within the EU, but also to the biofuel produced from raw materials sourced from non-European countries. In addition, each Member State shall ensure that the share of RES in the transport sector in 2020 will be at least 10% of the final consumption of energy in transport sector. To this end, each Member State must adopt national action plans to reach the share of RES consumed in transport, as well as in the production of electricity and heating, by 2020. The REDirective sets that biofuels should contribute to a reduction of at least 35% of GHG emissions in order to be taken into account to the 2020 goals.

According to the European Parliament press release, dated 11 September 2013, Members of the European Parliament have voted to adopt proposals which aim at reducing the environmental impact of biofuel production, particularly those resulting from indirect land use change (ILUC), by 2020. Among the proposals adopted are:

- The amount of food-based biofuels (first generation biofuels) should not exceed 6% of the final energy consumption in transport, as opposed to the current 10% target in existing legislation;
- Advanced biofuels, sourced from seaweed or certain types of waste, should represent at least 2.5% of energy consumption in transport;
- A 7.5% limit on ethanol in gasoline blends.

As a result of this recent discussion, the EU biofuel sector is currently under close scrutiny.

As already discussed in section 2.1, Europe is the most important producer and consumer of biodiesel fuels (Figure 2.1). In 2012, the share of biodiesel in the biofuels consumed by transport sector was 79%, while 20% corresponded to bioethanol and the remaining 1% to biogas (EurObserv'ER, 2013). Following the biofuel global trend, the biodiesel production over the EU was 12 times higher in 2011 than in 2000 (Figure 2.1).

The main European biodiesel producers in 2011 were Germany (33%), France (18%) and Spain (7%) (Figure 2.2). France is also the main bioethanol producer, contributing with 20% of the European bioethanol produced in 2011 and 24% in 2012 (Observ'ER, 2013). Despite the biggest slice of European biofuels is produced in Germany, France and Spain, is in the Slovak Republic where the incorporations of RES in road transports are higher (8.2%), followed by Austria (6.3%) and Sweden (6.1%). Spain, France and Germany are the following countries, and in the 9th position is Portugal with 5.3%. The EU-27 average incorporation of RES in transports was 4.7% (AEBIOM, 2013).

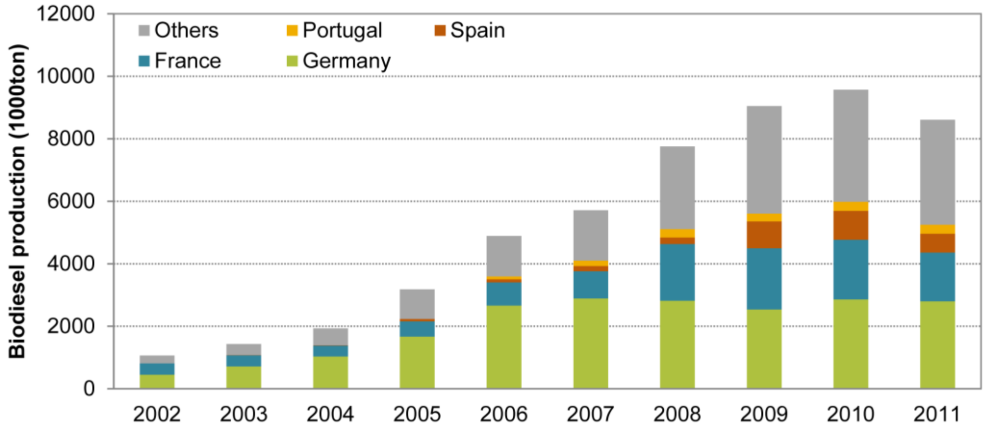


Figure 2.2 - Biodiesel production in Europe, Germany, France, Spain and Portugal, from 2002 to 2011 (URL 4)

Regarding the sustainability of biofuel used, the EurObserverv'ER survey (Observ'ER, 2013) points out that 61% of the total biofuel consumed across the EU-27 met the sustainability criteria in 2011 (100% in 13 countries) and it should be 82% in 2012 (100% in 15 countries). In Portugal, only 3% of the total biofuel used in 2011 is certified as sustainable, and it is estimated that this percentage increased to 4% in 2012 (Observ'ER, 2013).

2.3 The energy and transport sectors in Portugal

According to the EUROSTAT data referred to 2011 (EUROSTAT, 2013), Portugal was the seventh Member State of the EU-27 with higher energy import dependence (77.4%). Most of the imported energy is oil (46.1%), followed by gas (20.0%) and coal (9.9%). For the same year, the primary energy consumption was 30.1% higher than 1990. However, the consumption decreased 10.9% in the last decade (DGEG, 2013). This fact can be explained, in part, by the use of more efficient technologies and the investments on endogenous and renewable energy sources (like wind power), motivated by the Directive 2001/77/CE, from which Portugal has undertaken to produce a minimum amount of 39% of its gross electric power consumption from renewable sources by 2010.

In 2010, Portugal launched the National Strategy to Energy 2020 (ENE2020, MEID, 2010), driven by REDirective, aiming to reduce the energy external dependence to 74% by 2020, producing 31% of energy final consumption through endogenous sources (10% in transport sector), as well as increase the energy efficiency in 20% (39% in transport sector), among other objectives with relation to electric power. As a strategic document, the ENE2020 contemplates five axes:

1. Competitiveness, growth, energy and financial independence;
2. To bet on renewable energy sources (consubstantiated by National Action Plane for Renewable Energies – PNAER, 2010);
3. The promotion of energy efficiency through the National Action Plane for Energy Efficiency – PNAEE, 2008); 4) assurance safety supply;
4. Sustainability of energy strategy.

During the last two decades, Portugal has been making an effort to reduce external and fossil fuel energy dependence. In the 1990's the options were focused on coal, natural gas, hydroelectricity and biomass. With the ENE2020 (MEID - Ministério da economia inovação e desenvolvimento, 2010), Portugal has been focused on renewable energies such as solar, wind energy and biomass, including liquid biofuels to transport sector, reaching a share of RES of 24.6% of gross final energy consumption, in 2012 (EUROSTAT, 2014). Additionally, measures to reduce the energy consumption such as the use of more energy efficiency technologies have been seen as one of the most important strategies to achieve the EU's proposed goals.

In Portugal, the biggest slice of primary energy consumption is the oil: 60.0% (e/e) in 2000 and 49.3% (e/e) in 2011. The most important oil consumer is the transportation sector, accounting for 72% (e/e) of oil consumption and 35.5% (e/e) of total final energy consumption, in 2011 (DGEG, 2013). There are two main types of fossil fuels used by road transports: diesel and gasoline (liquid petroleum gas – LPG – is also used, however with a contribution lower than 0.5%, in energy basis). The share of diesel consumption on road transport has been increasing (Figure 2.3) from about 50% (e/e) between 1990 and 1995 to 70-76% (e/e) during 2006-2012.

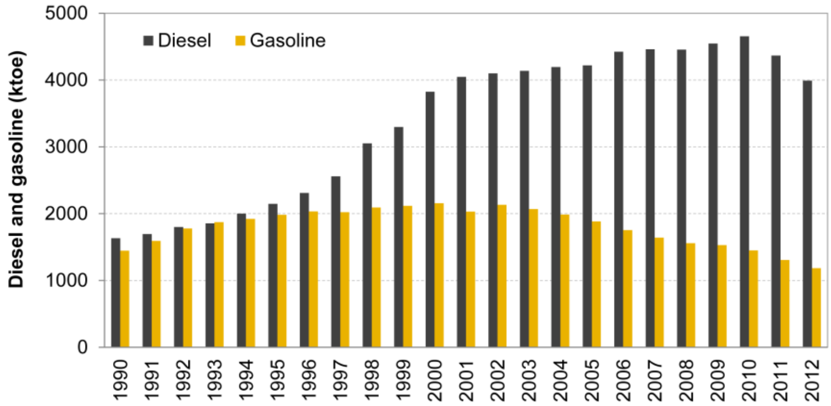


Figure 2.3 - Diesel and gasoline consumption (ktoe) by road transportation in Portugal, from 1990 to 2012 (URL 3).

Regarding GHG emissions, the transportation accounting for 24.8% (e/e) of total GHG emissions, which 96.8% (e/e) is referred to road transportation (IEA, 2013; APA, 2014). From 1990 to 2010, GHG emissions of the transport sector increased 84% (e/e) (APA, 2014), due to the steady growth of the vehicle fleet and road travel, in association with the increase in family income and the strong investment in road infrastructure in the 90s. The increase in road traffic activity also augmented the emissions from fossil fuel storage, handling and distribution. However, this situation has changed in the last years, and the transport emissions has started to decline in most recent years, caused by economic factors and the use of more efficient technologies (EEA, 2012; APA, 2014).

In 2006 (Decreto-Lei nº 62/2006, 21 March 2006), Portugal committed itself to replace 10% of conventional fuel for transport by biofuels in 2010, instead of 5.75% (in energy basis) as EU suggested, taking into account:

- The importance of the transport sector on the Portuguese energy budget;
- The fact that national transport sector consumes, presently, 76% (e/e) of diesel and 24% (e/e) of gasoline (Figure 2);
- The European environmental and energy concerns, namely regarding energy security and supply and climate change;
- The Directive 2003/30/EC.

However, Portugal was far to achieve the proposed goal: in 2008 the incorporation of biofuels on energy to transportation was 3.12% (e/e) (market statistics from Portuguese Association of Biofuels Producers (URL 6). With the launch of the REDirective in 2009, Portugal and all the Member State, have a goal of 10% of renewable energy in the transportation sector by 2020. Portugal intends to meet this goal with a contribution from biofuels, especially biodiesel (7.5% v/v), but also with a contribution of 2.5% (v/v) from bioethanol and a residual contribution from electric vehicles (Decreto-Lei nº 117/2010, 25 October 2010; MOBI.E, 2013).

Aligned with the European Roadmap 2050 (COM(2011) 112 final), which intends to reduce GHG emissions in 79-82% by 2050 (54-67% in transport sector), Portugal presented the national Roadmap for moving to a low-carbon economy in 2050 (APA – Agência Portuguesa do Ambiente, 2012). According to the modelling approach used to perform this roadmap, by 2030 the hybrid plug-in vehicles will begin to gain worth on light passenger transportation envisaging that the light passenger vehicle fleet will consist in 99% by hybrid plug-in vehicles and 1% by diesel vehicles (using a biodiesel blend) by 2050. On the other hand, the use of fuel with high biodiesel blends on heavy duty and passenger vehicles could represent an important slice on this sector (85%), followed by natural gas and fuel cells (APA, 2012).

2.4 Characterization of the Portuguese biofuels supply chain

Typically, the biofuels supply chain (Figure 2.4) comprises: the feedstocks production (energy crops); the feedstocks storage, handling and transportation to the biofuels production plants (or biorefinaries); the production processes, followed by the blending, the fuel distribution and finally the end use on road transport.

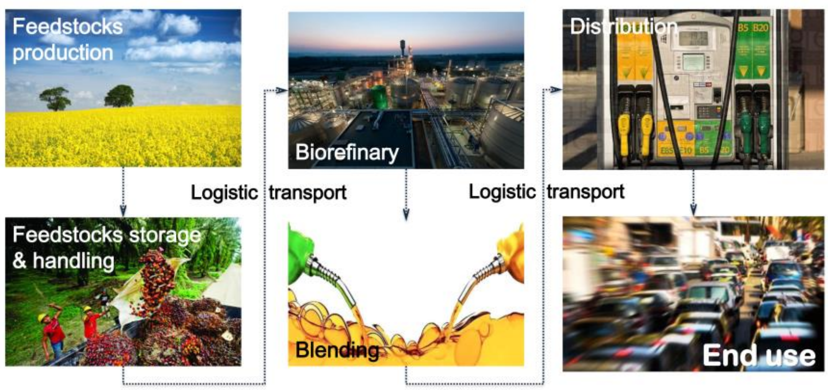


Figure 2.4 – Typical biodiesel supply chain.

A detailed description of each step is given following.

2.4.1 Raw material production and transportation

In the same year EU has published the biofuels Directive (2003/30/EC), it also established specific support schemes for producing energy crops in order to assist to the development of the sector (Council Regulation No 1782/2003), under the EU farm policy (*aka* Common Agricultural Policy – CAP). These support schemes includes an aid of 45 €.ha^{-1}.y^{-1} for areas sown under energy crops. In Portugal the aids started in 2007 for an area of 196 km^2 of plantation, but the number of farmers interested on aids to energy crops decreased 78% on the next year and 92% in 2009 (to 21.96 km^2 of plantation) (Figure 2.5).

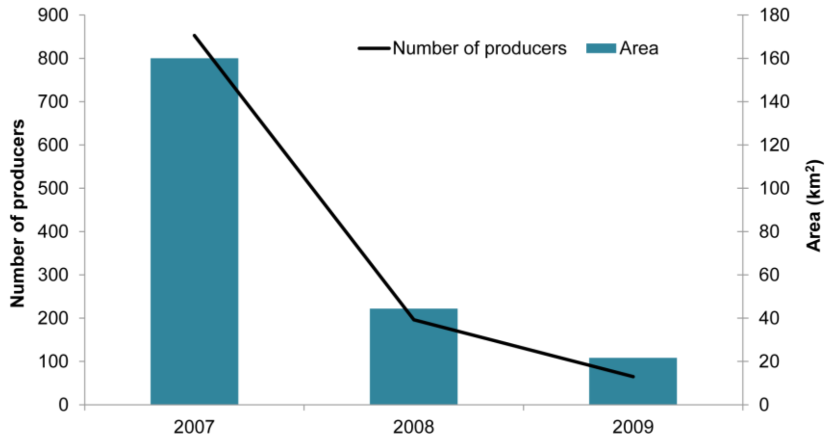


Figure 2.5 – Number of producers with aid to produce energy crops and respective cultivated area, from 2007 to 2009, in Portugal (URL 7).

According to statistical data from the Portuguese Laboratory for Energy and Geology (LNEG, URL 8), in 2007, Portugal used 183 kton of oil to biodiesel, being 3% from endogenous seeds (sunflower seeds), 82% from imported seed with national oil extraction (soybean and rapeseed), and the reminder 15% of the oil was directly imported (palm and rapeseed oil).

During this 3-years period of subsidized energy crops production, Portuguese farmers showed less and less attraction by bio-feedstocks cultivation, although there were five biodiesel production plants operating in national territory. Nowadays, sunflower crops in

Portugal are intended only for the food industry. From 2009 onwards there is no more endogenous cultivation of raw material for biofuels production.

Indeed, Portugal has some interesting land potential to produce energy crops to bioethanol (barley, wheat, maize and sugar beet), but it has not an interesting potential to produce oil crops to biodiesel (rapeseed, soybean, palm and jatropha) (Fischer et al., 2010). Moreover, an increase of the potential to produce advanced biofuels is not expected for Portugal (Fischer et al., 2010; Krasuska et al., 2010; Rettenmaier et al., 2010). Thereby, to import raw material (especially in grain basis) from the most important producers has shown to be more economic efficient. As Figure 2.6 shows, Portugal had been import soybean and rapeseed in oil and grain basis, as well as palm oil (Figure 2.6a,b), from Europe, America and Asia (Figure 2.7).

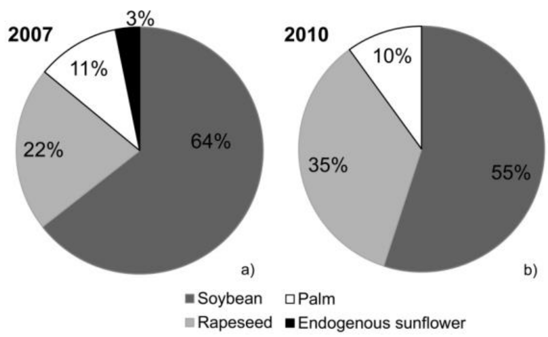


Figure 2.6 – Vegetable oil used to biodiesel production in Portugal in 2007 (a) and 2010 (b) (URL 9).

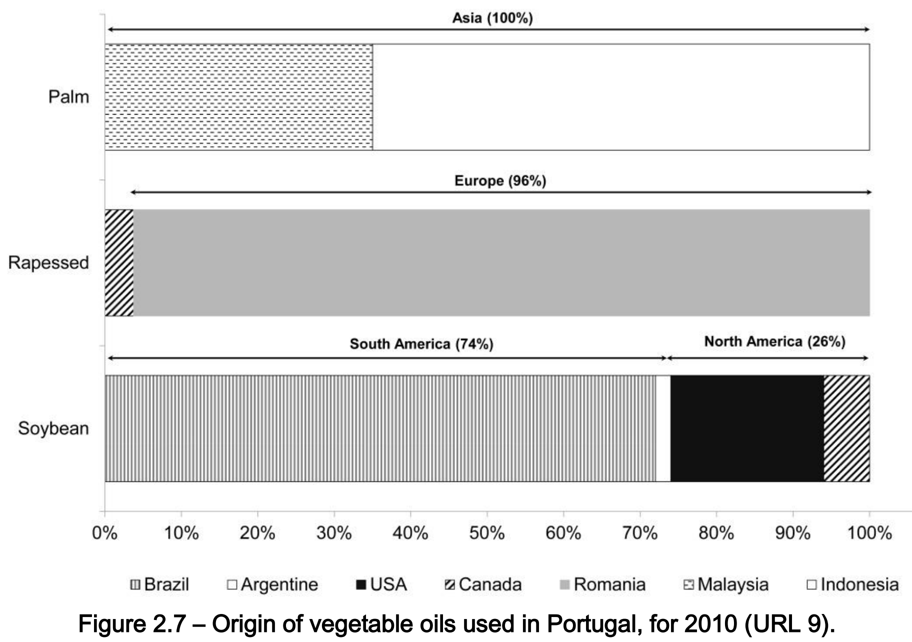


Figure 2.7 – Origin of vegetable oils used in Portugal, for 2010 (URL 9).

The statistical data suggests an increasing trend to the use of rapeseed oil from Europe and a trend to decrease the shares of palm oil and soybean from Asia and America, respectively, as well as the use of endogenous sunflower and rapeseed from Canada. In fact, there is an intention to shift towards the use of rapeseed from Europe over other feedstocks from non-European countries due to the cost associated to the raw materials transportation and to increase the sustainability of the biodiesel. According to the REDirective and life cycle assessment studies, soyabean has a worst environmental performance than rapeseed, namely in what concerns climate change (Sanz Requena et al., 2011).

Note that Figure 2.7 just presents the origin of vegetable oils used to biodiesel in 2010 because the 2010 picture is similar to 2007, except in what respect to rapeseed: in 2007, almost 100% of the rapeseed used was from Canada instead of Europe.

2.4.2 Biodiesel production

Portugal, motivated by the Directive 2003/30/CE, and taking advantage of national by-products from cattle feed industry, started to produce biodiesel derived from food sources (first generation biodiesel), in 2006. Beyond the commitment required by the Directive 2003/30/CE, biodiesel production was seen as a way to taking advantage of the vegetable oil, from the production process of food bran, namely soybean bran.

In 2006, two production plants (PP1 and PP2) initialized the biodiesel production with a total production capacity of 225 kton·y^{-1}. In the followed year, three more plants were implemented (PP3, PP4 and PP5), totalizing the actual production capacity of 550 kton·y^{-1} (the PP are geographically represented in Figure 2.7). There are other biodiesel producers in Portugal (APPB, URL 6), with a small dimension, but only these five are producing biodiesel in accordance with the EN 14214. They are also the founders of the Portuguese Association of Biofuel Producers that was created to tackle the challenges of the growing sector of biofuels and the lack of knowledge by the general public about the biodiesel market in Portugal.

Two of the production plants (PP1 and PP5) extract oil from seed (soybean, rapeseed and sunflower) to yield bran (no oil part), vegetable oil to food purpose, and biodiesel. All of the PP use a transesterification reaction between vegetable oil (soybean, rapeseed, sunflower and palm oils) and methanol, in the presence of a base catalyst (sodium or potassium hydroxides) to produce biodiesel. Glycerine is an important product of the transesterification reaction, with value for both pharmaceutical and cosmetic industries and all the glycerine is forwarded to these industries. However, information regarding the countries of destination and quantities exported are not known.

According to the General Direction for Energy and Geology (DGEG, URL 3), which is in charge to make the annual energy budget for Portugal, the biodiesel produced in Portugal is only used internally. Additionally, there are not records of biodiesel importation in this period.

The biodiesel production and incorporation have increased from 91 000 m^3 in 2006 to 384 000 m^3 in 2011, being the maximum production registered to 2010 (441 000 m^3) (URL 3 and URL 6).

2.4.3 Biodiesel/diesel blending

From 2006 to present, the national biodiesel production has been increasing as well as its incorporation in diesel, in order to fulfil the EU targets (Figure 2.8).

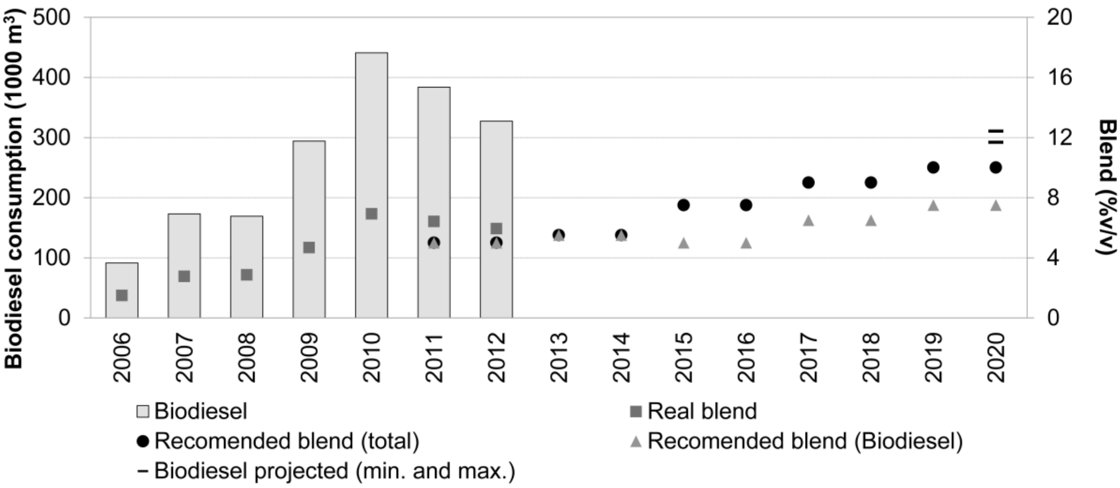


Figure 2.8 – Biodiesel consumption and blends really used from 2006 to 2011. Recommended biofuel and biodiesel blends until 2020 and biodiesel blend projected by 2020. The data are related to Portugal (MEID, 2010; URL 3 and URL 6).

According to Figure 2.8 it is noticed that the targets for 2011 (5% v/v), proposed by Directive 2009/28/EC and imposed by national law (DL 117/2010) were accomplished

(6.99% v/v). The actual level of biodiesel incorporation must be kept at 7% (v/v) until 2019 and then it should be increased to 7.5% (v/v), at least (but maximum incorporation of biodiesel allowed by EN 590:2009 is 7% v/v). Moreover, the substitution of 2.5% v/v of gasoline by bioethanol is expected from 2015 onwards. With both biofuels contribution, the transport sector would account for 10% (e/e) of energy from non-fossil sources.

2.4.4 Transport and distribution associated to the national biodiesel supply chain

The main infrastructures related to the biodiesel supply chain, namely the harbours of Lisbon and Aveiro, the petroleum refineries at Sines and Matosinhos and the biodiesel production plants (PP1-5), are represented in Figure 2.9. Additionally, the main railway and highways are also presented in Figure 2.9.

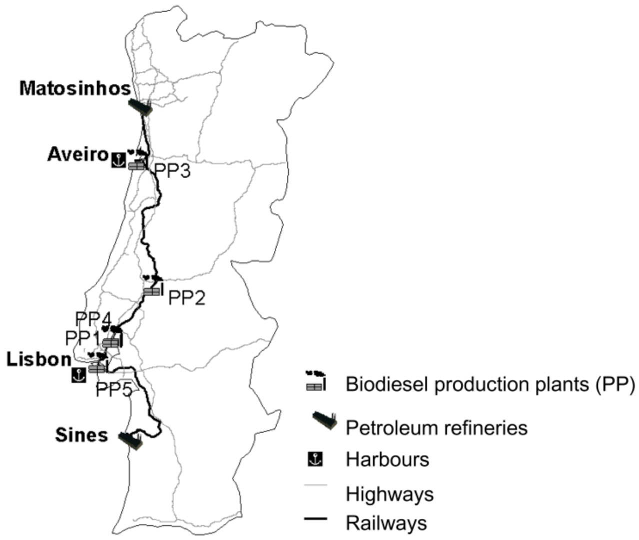


Figure 2.9 – Biodiesel production plans, petroleum refineries, main communication lines and harbours.

The raw materials enter into Portugal through the harbours of Lisbon and Aveiro. Then, they are distributed to the PP1 and PP4 by roadway and by railway to PP2. The distribution of raw materials to PP3 and PP5 are directly made from the harbours.

The vegetable oil is converted to biodiesel in each PP and it is distributed to the petroleum refineries at Sines and Matosinhos in order to perform the fuel blends. This transportation is carried out by shipping and train. The quantities of biodiesel forward to each petroleum refinery are not known. However, it is known that the Refinery of Sines produces 65-70%

(v/v) of diesel at national level and the remaining comes from Matosinhos (Galp, 2012a, 2012b).

Hereupon, the biodiesel production implies a significant increase of shipping traffic due to the raw material importation. As a consequence, there are atmospheric pollutants and GHG emissions associated to this logistics. According to Jonson et al. (2009) emissions from international shipping in sea areas surrounding Europe contribute about 30% of the EU27 emissions of SOx and NO and affect ozone levels all over Europe.

The blend distribution to the final consumer follows the same path as others petroleum derivate. For this purpose there is a pipeline connecting Sines and the fuel storage facility located nearby PP1 and PP4. The total storage capacity is approximately 350 000 m^3 of which 315 000 m^3 for diesel/biodiesel, gasoline and jet, and 30 800 m^3 for LPG. The facility is equipped with a loading station for liquid fuels with capacity for 10 tanker trucks. The distribution of diesel/biodiesel blends for all the fuel station scattered across national territory is carried out by the tanker trucks.

2.5 Discussion and final remarks

In Europe, biofuels have been pursued as a potential way to reduce the use of petroleum-based fuels and the emission of GHG as well, which have been a source of concern for the EU. With the REDirective (2009/28/EC), which replaced the 2003/30/EC directive, specifics targets on the promotion of renewable energy sources use in transport sector by 2020 and sustainability criteria for biofuels were established. According to more recent intentions from Members of the European Parliament, a new directive will be published to promote advanced biofuels, limiting the production and use of first generation biofuels to minimize biofuel impacts on environment and socio-economy (ILUC impacts).

In Portugal, the production and use of biodiesel started in 2006 and the current biodiesel supply chain is characterized by:

- The importation of grain and vegetable oil (rapeseed, soybean and palm) from Europe, Asia and America;
- The national extraction of a part of the vegetable oil from imported seeds,
- The production of the total amount of biodiesel (production capacity of 550 $kton \cdot y^{-1}$);

- A vast transport operations of raw materials from the origin countries to national harbours and then to biodiesel production plants, and finally the transport of biodiesel to petroleum refineries.

Besides biofuels are seen as one of the ways to reduce energy external dependence of the developed countries as well as to decrease GHG emissions, the Portuguese strategies and policies related to biofuel issues are only focused on the biofuels production and end-use. Moreover, the biodiesel supply chain has problems of sustainability due to its dependence on the raw materials importation from Europe, Asia and America.

To address the importance of biofuels on national economy and the perspectives of this sector, meetings were organized involving experts and national stakeholders. Some conclusion and guidelines for decision makers came out from these meetings, namely:

- Portugal has some interesting land potential to produce energy crops for bioethanol (barley, wheat, maize and sugar beet), but the same is not true for oil crops production for biodiesel (rapeseed, soybean, palm and jatropha), except sunflower. Additionally, there is just a few amount of area available for energy crops. Thereby, the importation of raw material from the most important producers has shown to be more economically efficient;
- The importation and internal transportation of raw materials and biodiesel leads to atmospheric pollutant and GHG emissions increase. In this sense, the Portuguese energy policies and strategies related to biofuels are neither contributing to the reduction of external energy dependence nor to balance the GHG emitted from the biodiesel supply chain. Moreover, only 4% of the total biofuel consumed in Portugal was certified as sustainable according to the criteria defined by the REDirective. Therefore some additional measures/actions should be considered to define a more sustainable biofuels strategy for Portugal integrated with European strategies;
- The risk of food-energy competition should be discarded by favouring the use of residues from other industries, such as the food industry, on biofuels production;
- European and national law established that by 2015 a 2.5% share of bioethanol should be incorporated in gasoline. Portugal has an interesting land potential to produce energy crops for bioethanol, these crops should be actively promoted as an opportunity for rural development by incorporating agriculture in the energy market, generating jobs and incomes;

Recognizing some sustainability problems of the national biodiesel supply chain in terms of biodiesel feedstocks origins, the APPB launched, in July 2013, a campaign to promote national energy crops production based on food feedstocks to biodiesel (http://www.biodiesel.pt/), claiming that it is a challenge to increase investment in biodiesel production reducing, at the same time, the cost associated to the soyabean-based animal feed chain. More than one year after the release of this campaign no progress reports are known.

In order to successfully incorporate biofuels, additional information is required regarding their environmental impact, especially nowadays that the introduction of advanced biofuels is being debated. Additionally to the use of biofuels for transportation, these advanced biofuels should be promoted in other sectors. At the national industry level, several studies have been performed in order to convert by-products and/or industrial residues to biofuels for use in the industrial process itself (Carvalho et al., 2010b; Dias et al., 2012; Fernandes and Gaspar, 2012).

Chapter 3. Atmospheric pollutant emission related to biofuels use in road transports

An extended literature review regarding engine performance and the effects on atmospheric pollutant emissions when diesel/biodiesel blends are used as fuels on EURO 3-4 light passenger vehicles constitutes the first part of this chapter. Two main groups of atmospheric pollutants were analysed: regulated pollutants (CO, CO_2, PM10, PM2.5, NOx and NMVOC) and non-regulated pollutants (formaldehyde, acetaldehyde, benzene and acrolein). Moreover, to against to the lack of information an experimental work was conducted aiming the study of exhaust gases emissions from a EURO 5 light passenger vehicle.

3.1 Effects of biodiesel on emissions

Over the last years, several studies have been published regarding engine performance and the effects on atmospheric pollutant emissions when biodiesel is used as pure or blend fuel. Based on the these studies, the review developed by Xue et al. (2011) points out that the blend fuels with small content of biodiesel in place of petroleum diesel can help in controlling air pollution and easing the pressure on scarce resources without significantly sacrificing engine power and economy. The effect of biodiesel on performance and exhaust emissions (Figure 3.1) depends on the type of engine, engine speed, load conditions, ambient conditions as well as biodiesel quality and feedstocks. These are parameters on which the engine performance and emissions assessment and analysis should be based.

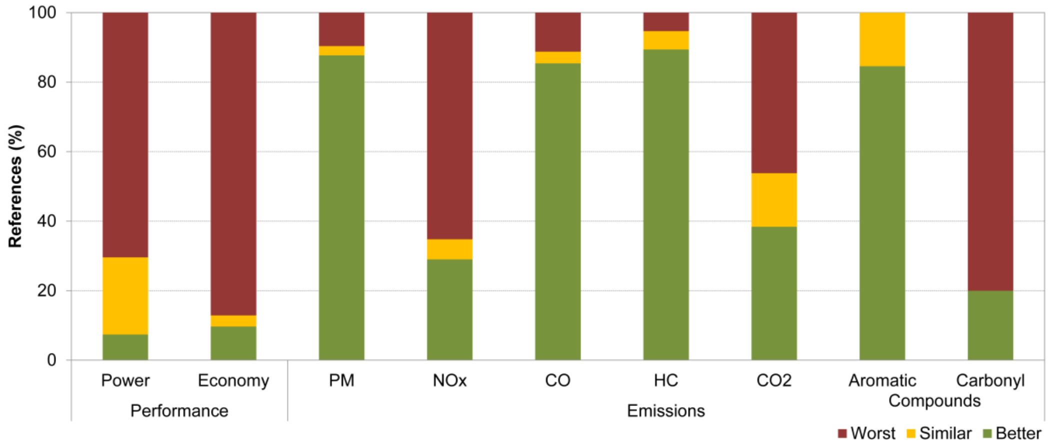


Figure 3.1 – Research work conclusions regarding the effects of biodiesel on engine performance and emissions with respect to pure diesel, beyond 2000 (adapted from Xue et al., 2011).

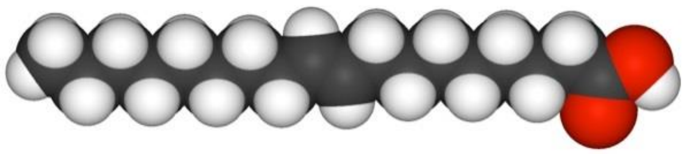
The biodiesel quality is highly depend on physical and chemical properties of the fuel (Table 3.1), which are also dependent on the feedstock characteristics (Kumar and Chauhan, 2013).

Table 3.1 – Physical and chemical specifications regarding biodiesel and diesel fuels (from: Bakeas et al., 2011; Ayhan Demirbas, 2009; Gupta and Demirbas, 2010; Lapuerta et al., 2008; Lin and Fan, 2011).

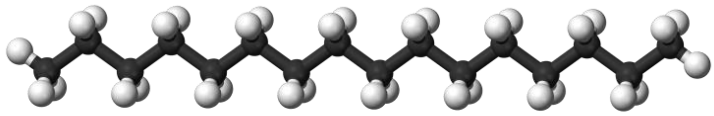
Parameter	Biodiesel	Diesel
Density (kg·m^{-3}), at 15 ºC	860-895	810-860
Viscosity (mm^2·s^{-1}), at 40 ºC	3.3-5.5	2-3.5
Cetane number	45-65	40-55
Flash point	120-180	55-63
Heating value (MJ·kg^{-1})	39-41	46
Water content (mg·kg^{-1})	0-500	<50
Acid number (mg KOH·g^{-1})	<0.60	-
Ester content (% m·m^{-1})	>96	-
Glycerine content (% m·m^{-1})	<0.25	-
Sulphur content (mg·kg^{-1})	≈0	15-500 (<10 in the EU)

More than 70% of the literatures consulted by Xue et al. (2011) (Figure 3.1), suggest that engine power drop with the increasing of biodiesel content due to the loss of heating value of biodiesel. According to Lin et al. (2009) and Öner and Altun (2009), higher viscosity of biodiesel, enhancing fuel spray penetration, improves air-fuel mixing and thus recovers the torque and power losses and improves the combustion efficiency as well, due to the lubrication improvement of the injection metallic components of the engine (Lopes et al., 2014). The use of biodiesel also leads to reductions on PM, CO, HC and aromatic compounds emissions, while the NOx and carbonyl compounds emissions usually increase (Figure 3.1). These variations on emissions are mainly related to the biodiesel content, the cetane number, the aromatic and oxygen contents, and the physic characteristics of biodiesel, namely viscosity and density (e.g. Bakeas et al., 2011; Karavalakis et al., 2011; Lapuerta et al., 2008; Lopes et al., 2014; Randazzo and Sodré, 2011; Tan et al., 2012; Xue et al., 2011).

The molecular structure of biodiesel (e.g. $C_{19}H_{36}O_2$, elaidic acid methyl ester, Figure 3.2a) differs from that of conventional diesel (e.g. $C_{16}H_{34}$, hexadecane, Figure 3.2b). Typically, biodiesel is a fatty acid methyl ester (FAME) containing oxygen atoms, and they could have simple (saturated) or double bounds (monounsaturated or polyunsaturated) within fatty acid chain with between 12 and 22 carbon atoms long. Conventional diesel is a linear alkane with a shorter carbon chain (8-21 carbon atoms) than biodiesel. The molecular structure of the fatty acids strongly influences the biodiesel properties such as ignition quality, cold flow, oxidative stability, viscosity and lubricity (Kumar and Chauhan, 2013).



a) Elaidic acid methyl ester ($C_{19}H_{36}O_2$)



b) Hexadecane ($C_{16}H_{34}$)

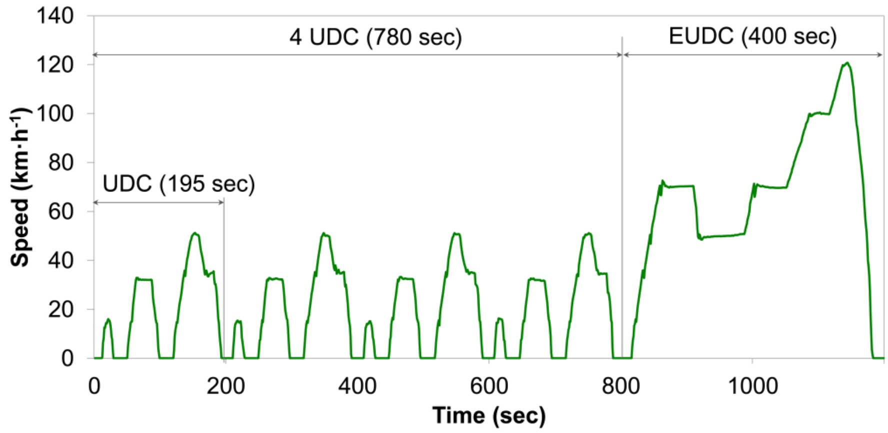
Figure 3.2 – Molecular structure of a biodiesel a) and a conventional diesel b). Carbon, hydrogen and oxygen atoms are represented as grey, white and red bools, respectively.

One of the most important differences between biodiesel and conventional diesel is the oxygen content. Biodiesel has 10-12 %(m/m) oxygen while diesel does not have it. In this sense, lower CO, PM and VOC emissions, but higher NOx emissions are expected from biodiesel when compared to diesel (Demirbas, 2009; Gaffney and Marley, 2009; Gupta and Demirbas, 2010; Krahl et al., 2001; McCormick et al., 2006; Serrano et al., 2011; Taylor, 2008; Xue et al., 2011).

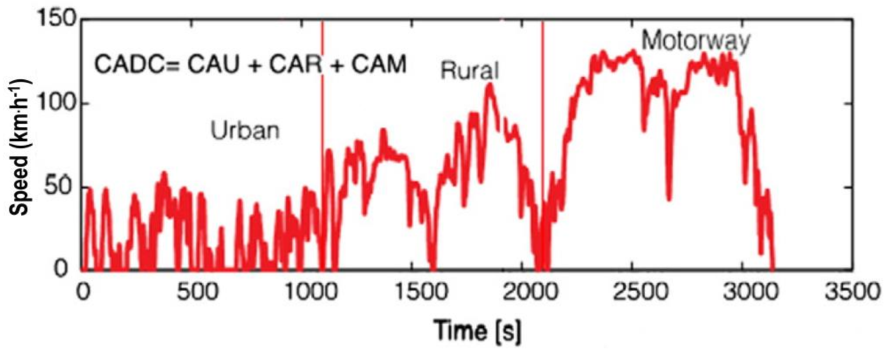
It is commonly accepted that the use of biodiesel instead of diesel decreases the engine power (Figure 3.1). This fact is attributed to the lower heating value of biodiesel, which means that biodiesel fuels release less energy for producing work. In some literatures (Monyem et al., 2001; Lin et al., 2009; Öner and Altun, 2009) are reported that the recovery in torque and engine power for biodiesel is possible due to its higher viscosity, which can play an important role in improving the lubrication of the injection metallic components of the engine, enhancing fuel spray penetration, improving air-fuel mixing, and then increases combustion efficiency (Ramadhas et al., 2005; Lopes et al., 2014). However, if fuel viscosity reaches a very value of viscosity it could decrease combustion efficiency due to bad fuel injection atomization (Utlu and Koçak, 2008; Wu et al., 2009; Aydin and Bayindir, 2010a).

Other fuel characteristic that usually is pointed out as an advantage for biodiesel is its high cetane number. Cetane number, only used for the relatively light distillate diesel oils, is a measure of the time period between the start of ignition and the first identifiable pressure increase during combustion of the fuel (fuel's ignition delay). Thus, it is an indicator of the combustion quality of diesel fuels during the compression ignition. Higher cetane number fuels, like biodiesel, have shorter ignition delay periods than lower cetane number fuels, like diesel. Minimize this delay, and so increasing cetane number, results in less unburned fuel in the cylinder and more efficient combustion process. Thus, the use of biodiesel instead of diesel, generally leads to a quick burning and to lower premixed combustion, which provides softer changes in pressure and temperature. Accordingly, the use of a high cetane fuel results in less PM (e.g. Kidoguchi, 2000; Korres et al., 2008; Kwanchareon et al., 2007), CO (e.g. Kumar et al., 2009; Wu et al., 2009), HC emissions (e.g. Wu et al., 2009) and NOx (namely NO, Wu et al. (2009) and EPA, (2002)).

As mentioned above, emissions are strongly influenced by the driving cycle. The kinematic profile of the driving cycles is a major factor in the measured emission representatively (Fontaras et al., 2009). Therefore, driving cycles were established to assess the performance of vehicles namely in terms of fuel consumption and pollutant emissions. The most important driving cycles defined to Europe driving conditions are New European Driving Cycle (NEDC, Figure 3.3a) and the Common Artemis Driving Cycle (CADC, Figure 3.3b).



a)



b)

Figure 3.3 – Speed profile of the a) NEDC and b) CADC (Fontaras et al., 2014).

The NEDC, described in detail by the Directive 70/220/EEC and further amendments, represents the typical usage of a car in Europe and it is designed to assess the emission levels of car engines and fuel economy in passenger cars. It is constituted by two different cycles (Figure 3.3a): the first one is known as Urban Driving Cycle (UDC), and the second one is defined as Extra-Urban Driving Cycle (EUDC). In the UDC the vehicle is driven through 1 013 m at an average speed of 18.7 km·h^{-1} during 195 s. This routine is repeated four times in a sequence, totalizing 4 052 m in 780 s. The urban driving conditions are characterized by low speed, low engine load, and low exhaust gas temperature. In contrast, the EUDC, in the second part of the NEDC, accounts for extra-urban and high speed driving modes up to a maximum speed of 120 km·h^{-1}. The vehicle has an average speed of 62.6 km·h^{-1} and it takes 400 s to move through 6955 m. The entire NEDC covers a distance of 11 007 m in a time period of 1 180 s and at an average speed of 33.6 km·h^{-1}.

However, the NEDC has been criticised for not being representative of real-world vehicle operation (Dings, 2013). Therefore, the CADC (Figure 3.3b) was developed to simulate a real-world driving cycle, representing average driving conditions in Europe (André, 2004). It was specifically designed for emission modelling purposes. This driving cycle is distinguished into an urban (CAU), a rural (CAR), and a motorway (CAM) part, each representative of the corresponding driving condition.

Based on literature review, including experimental procedures under NEDC and CADC, the effects of biodiesel on road transports emissions including regulated and non-regulated pollutants are surveyed and analysed throughout this section.

3.1.1 NOx

Nitrogen oxides (NOx) is a generic term for nitric oxide (NO) and nitrogen dioxide (NO_2). They are mainly produced from the combustion reaction, especially at high temperatures, when nitrogen (N_2) from the air combines with oxygen (O_2) also from the air or from the oxygenated fuel. The burning of fossil fuels, namely on road transport sector, is the main anthropogenic source of NOx. Besides NOx emissions from the road transport sector has decreased almost 40% over the last two decades in Europe (EEA, 2013), this sector is still the main source of this pollutant emissions, representing 46% of NOx total emissions in Portugal (APA - Agência Portuguesa do Ambiente, 2011) and 41% in Europe (EEA, 2013).

As represented in Figure 3.1, more than a half of the research studies suggest that the use of biodiesel causes increases on NOx emissions (Xue et al., 2011). This increase is mainly due to higher oxygen content of biodiesel. However, the effects of oxygenated fuel blends on NOx emissions is complex and there is no unanimity among the experimental studies performed over the last years (Lapuerta et al., 2008; Bakeas et al., 2011; Karavalakis et al., 2011a; Xue et al., 2011; Kumar and Chauhan, 2013). According to Kalligeros et al. (2003), reducing the ignition delay by increasing the cetane number drives to a lower NOx formation rate since the combustion pressure rises slowly, giving more time for cooling through heat transfer. Then, higher cetane number leads to lower localized gas temperature, minimizing the NO formation by thermal reactions. Additionally, saturated ester are pointed out to have higher cetane number than unsaturated esters (Canakci and Gerpen, 2001; Knothe, 2014), and then the saturation level of the fatty acids also leads to decrease of the NOx emissions (Wyatt et al., 2005; Knothe et al., 2006; Lin et al., 2009).

Engine load also plays an important role on the NOx formation mechanism. NOx increases as load is increased, as a result of higher combustion temperature during the high engine load (Bakeas et al., 2011; Xue et al., 2011). The low speed and load imposed by an urban driving cycle are the main reasons for the decreasing trend of NOx emission with the increase of biodiesel content (Gumus and Kasifoglu, 2010; Zhu et al., 2010; Xue et al., 2011; Lopes et al., 2014).

Modern internal combustion engine vehicles have been recently using the exhaust gas recirculation (EGR) technique to reduce NOx emission by recirculating a portion of an engine's exhaust gas back to the engine cylinders. The use of this technique is the main reason for the decrease of NOx emission found for modern vehicles, and when biodiesel is used the reduction is more effective (Tsolakis et al., 2007). However, EGR rates are optimized to match the operating conditions of diesel. Therefore, EGR rates may need adjustments due to the change of the combustion characteristics of each biodiesel blends (Xue et al., 2011).

The NOx emission variations from the biodiesel use on diesel vehicles are presented in Table 3.2, for EURO 3 (EMEP/EEA, 2013) and EURO 4.

Table 3.2 – Effects of biodiesel blends on diesel vehicle NOx emissions for EURO 3 (EMEP/EEA, 2013) and EURO 4 (Bakeas et al., 2011) vehicles.

European emission standards	Vehicle type	B10	B20	B30
EURO 3 (under NEDC)	Passenger vehicles	0.4%	1.0%	-
	Light commercial vehicles	1.7%	2.0%	-
	Heavy-duty vehicles	3.0%	3.5%	-
EURO 4 (under NEDC and CADC)	Passenger vehicles	2.1%	5.9%	9.3%

3.1.2 Particulate matter (PM)

Particulate matter is mainly composed by dry soot, sulphate and soluble organic fraction (SOF) (Chen et al., 2007). Due to the higher oxygen content, the low (or inexistent) levels of sulphur content and higher cetane number of biodiesel, it is an overwhelming argument that the PM emissions decrease with the use of biodiesel instead of diesel (Lapuerta et al., 2008; Xue et al., 2011; Kumar and Chauhan, 2013). However, the reductions in PM emissions have been shown as being more effective with lower diesel concentrations in the blends, mainly due to the high viscosity that characterize biodiesel, which may cause a worse fuel atomization and volatilization processes, and further deteriorate the combustion quality (Senthil Kumar et al., 2003; Turrio-Baldassarri et al., 2004; Banapurmath and Tewari, 2008; Song and Zhang, 2008a; Wu et al., 2009; Aydin and

Bayindir, 2010b; Qi et al., 2010). Moreover, according to Armas et al. (2010), the increasing of PM emissions can also occur due to the unburned or partly unburned HC compounds that condensate and be absorbed on the PM surface, increasing the SOF (the main component of PM in exhaust gases).

PM are formed in the locally rich regions of the heterogeneous mixture of fuel and air during combustion in the combustion chamber. Further air-fuel mixing results in burning of PM at the boundary of diffusive flame due to the high temperature and available oxygen at the region. The increase of oxygen content in the fuel contributes to a complete fuel oxidation even in locally rich zones and it is also leads to a significant decrease in PM emissions and smoke (Lapuerta et al., 2008). The high cetane number of biodiesel is another reason to justify the reduction of PM emissions, due to its contribution on combustion efficiency improvement (Kwanchareon et al., 2007; Song and Zhang, 2008b; Nabi et al., 2009).

The PM emission variations from the biodiesel use on diesel vehicles are presented in Table 3.3, for EURO 3 (EMEP/EEA, 2013) and EURO 4.

Table 3.3 – Effects of biodiesel blends on diesel vehicle PM emissions for EURO 3 (EMEP/EEA, 2013) and EURO 4 (Bakeas et al., 2011) vehicles.

European emission standards	Vehicle type	B10	B20	B30
EURO 3 (under NEDC)	Passenger vehicles	-13.0%	-20.0%	-
	Light commercial vehicles	-15.0%	-20.0%	-
	Heavy-duty vehicles	-10.0%	-15.0%	-
EURO 4 (under NEDC and CADC)	Passenger vehicles	-0.7%	-3.4%	-5.8%

3.1.3 CO and HC

According to up to 84% of the consulted literatures, CO emissions are reduced when diesel is replaced by biodiesel (Figure 3.1). Similar to CO, almost 90% of the literature points out that the use of biodiesel instead of diesel reduces HC emissions (Figure 3.1). This is mainly due to the oxygen content of biodiesel, that promotes a more complete combustion, and its higher cetane number that contributes to lower possibility of formation of rich fuel zone, and then less CO emissions (Xue et al., 2011; Kumar and Chauhan, 2013). Additionally, according to Abd-Alla et al. (2001), higher cetane number of biodiesel could reduce the burning delay, which results in the total HC emissions reduction. Nevertheless, experimental studies have shown that the lower biodiesel concentration is more effective than the higher one in terms of HC emissions, because higher reduction in HC emissions appeared with the low content of biodiesel (up to 50%) (Song and Zhang, 2008b; Ghobadian et al., 2009).

Experimental results (Ramadhas et al., 2005; Gumus and Kasifoglu, 2010) justify that the differences in CO emissions for biodiesel and diesel fuels at high load is caused by the oxygen content, but at low load they point out to the high cetane number. Actually, engine load has been proven to have a significant impact on CO emissions. There is an unanimous conclusion about the effect of engine speed on CO emissions: they decrease with an increase in engine speed (Xue et al., 2011). Regarding the engine load and HC emissions, the compiled existing studies lead to inconsistent conclusions (Xue et al., 2011).

Knothe et al. (2006) reported that CO and HC emissions reduced with the increasing of the chain length after tested on an engine with lauric (C12:0), palmitic (C16:0) and oleic (C18:1) methyl ester. Indeed, feedstocks of biodiesel affect CO and HC emissions, as well as the combustion process, since cetane number increase with decreasing unsaturation and increasing chain length, which are influenced by biodiesel feedstock, oil processing technology and climate condition of the area where oil is collected (Ramadhas et al., 2006; Kumar and Chauhan, 2013).

Nevertheless, some authors have reported a significant increase in CO emissions for pure biodiesel and also for blend fuels (Banapurmath and Tewari, 2008; Fontaras et al., 2009; Sahoo et al., 2009). The main reasons given by the authors are related to the higher viscosity and poor spray characteristic for biodiesel, which lead to poor mixing and poor combustion conditions.

The CO and HC emission variations from the biodiesel use on diesel vehicles are presented in Table 3.3, for EURO 3 (EMEP/EEA, 2013) and EURO 4.

Table 3.4 – Effects of biodiesel blends on diesel vehicle CO and HC emissions for EURO 3 (EMEP/EEA, 2013) and EURO 4 (Bakeas et al., 2011) vehicles.

Pollutant	European emission standards	Vehicle type	B10	B20	B30
CO	EURO 3 (under NEDC)	Passenger vehicles	0.0%	-5.0%	-
		Light commercial vehicles	0.0%	-6.0%	-
		Heavy-duty vehicles	-10.0%	-9.0%	-
	EURO 4 (under NEDC and CADC)	Passenger vehicles	-7.5%	-17.0%	-22.6%
HC	EURO 3 (under NEDC)	Passenger vehicles	0.0%	-10.0%	-
		Light commercial vehicles	-10.0%	-15.0%	-
		Heavy-duty vehicles	-10.0%	-15.0%	-
	EURO 4 (under NEDC and CADC)	Passenger vehicles	-3.4%	-8.1%	-12.3%

3.1.4 CO_2

Carbon dioxide is an important GHG especially due to the huge amount emitted by anthropogenic sources (electricity generation, industrial and domestic combustion and transportation) worldwide. One of the main motivations for the use of biofuels, namely biodiesel, in the transport sector is the reduction of these GHG emissions.

All the published works that study the effects of biodiesel on engine performance and exhaust gases emissions include CO_2. However, their conclusions vary considerably (Figure 3.1). On one hand, some authors suggest that the use of biodiesel generates more CO_2 emissions than pure diesel. This increase is mainly due to the presence of oxygen into the biodiesel molecules, promoting a more complete combustion (Lin and Lin, 2007; Utlu and Koçak, 2008; Chauhan et al., 2012). On the other hand, some researches have reported that the high viscosity of biodiesel reduces cone angle which leads to the reduction of the amount of air available for the combustion process, resulting in hindrance to complete the combustion reaction (Gumus, 2008; Mani et al., 2009). Thus, contrarily to other pollutants, CO_2 emission increase as more efficient is the combustion reaction. Nevertheless, the increase of CO_2 emissions is not a concern due to nature's recovery by raising biodiesel crops and by decreasing of production of petroleum-based diesel. Thus, the effect of biodiesel on CO_2 emissions should be performed through life cycle assessment (LCA) methodologies (Nanaki and Koroneos, 2012). There are several published studies that evaluate the effect of biodiesels on global greenhouses gases emissions through the LCA, which have pointed out that biodiesel can cause a 50-80% reduction in CO_2 emissions compared to petroleum-based diesel, regarding each fuel life cycle, considering biodiesel feedstocks as endogenous (Malça and Freire, 2011; Kumar et al., 2012; Nanaki and Koroneos, 2012).

The CO_2 emission variations from the biodiesel use on diesel vehicles are presented in Table 3.3, for EURO 3 (EMEP/EEA, 2013) and EURO 4.

Table 3.5 – Effects of biodiesel blends on diesel vehicle PM emissions for EURO 3 (EMEP/EEA, 2013) and EURO 4 (Bakeas et al., 2011) vehicles.

European emission standards	Vehicle type	B10	B20	B30
EURO 3 (under NEDC)	Passenger vehicles	-1.5%	-2.0%	-
	Light commercial vehicles	-0.7%	-1.5%	-
	Heavy-duty vehicles	0.2%	0.0%	-
EURO 4 (under NEDC and CADC)	Passenger vehicles	0.4%	1.1%	1.6%

3.1.5 Non-regulated pollutants

Beyond basic regulated pollutants, several measurements on non-regulated pollutants emitted by road transports have been recently performed (Xue et al., 2011), most concentred on the composition and quantification of HC and PM (Peng et al., 2012). These include quantification of volatile organic compounds (VOC) and carbonyl compounds (aldehydes) from gaseous exhaust and measurements of aromatic and polyaromatic hydrocarbons (PAH) from both gaseous and particulate emissions. The interest on these pollutants are mainly because they are hazardous for human health and environmentally dangerous (Peng et al., 2008).

The existing studies point out that exhaust emissions are lower in total VOC, total carbonyl compounds and total PAH when biodiesel blends are used (Corrêa and Arbilla, 2008; Peng et al., 2008; Macor et al., 2011). However, the same studies reveal that the ratio of total VOC to HC increase with the biodiesel concentration and the soluble organic fraction of the emitted PM is greater in biodiesel exhaust emissions that it is in diesel's, even though the reduction are shown in total HC and total mass of PM for biodiesel.

3.1.5.1 Carbonyl compounds

Carbonyl compounds (CC) belongs to a class of substances produced by the partial oxidation of the hydrocarbons, which appear in intermediate phases of the combustion process (Lapuerta et al., 2008). Aldehydes and ketones are the CC more frequently studied in diesel exhaust.

Due to its adverse health effects, such as eyes respiratory system and irritation, and carcinogenicity, carbonyl compounds are drew the public's and research's attention. Moreover, they are also precursors of photochemical smog (Bakeas et al., 2003; Macor et al., 2011). In urban areas, most of the aldehyde emissions are from automotive exhaust (Bakeas et al., 2003; Jacobson, 2007). Therefore, the effects of biodiesel fuel on these emissions are important for urban air quality and human health.

Besides the discordant results for biodiesel regarding carbonyl compounds emissions, it is widely accepted and proved by 80% of the experimental works consulted by Xue et al. (2011) (Figure 3.1), that biodiesel increases these emissions as a consequence of the oxygen content in the molecule. Corrêa and Arbilla (2008) found that all carbonyl emissions exhibit a strong correlation (correlation coefficients of 0.96) with the biodiesel content (B2, B5, B10, B20), which indicates that the biodiesel ester molecules are probably the source of these carbonyls. Liu et al. (2009) detected that exist a weaker correlation between the biodiesel content (B10, B30, B50, B75, B100) and the carbonyl compounds, partially due to the fact that the engine used was designed to run on diesel. Carbonyl compound emissions are also influenced by the driving cycle.

The effects of the use of biodiesel blends on CC emissions were analysed by Karavalakis et al. (2011b), regarding an EURO 4 light passenger vehicle. The carbonyl compound emission factors found for each fuel over the NEDC and the three phases of the CADC (urban-CAU, road-CAR and motorway-CAM) are shown in Figure 3.4.

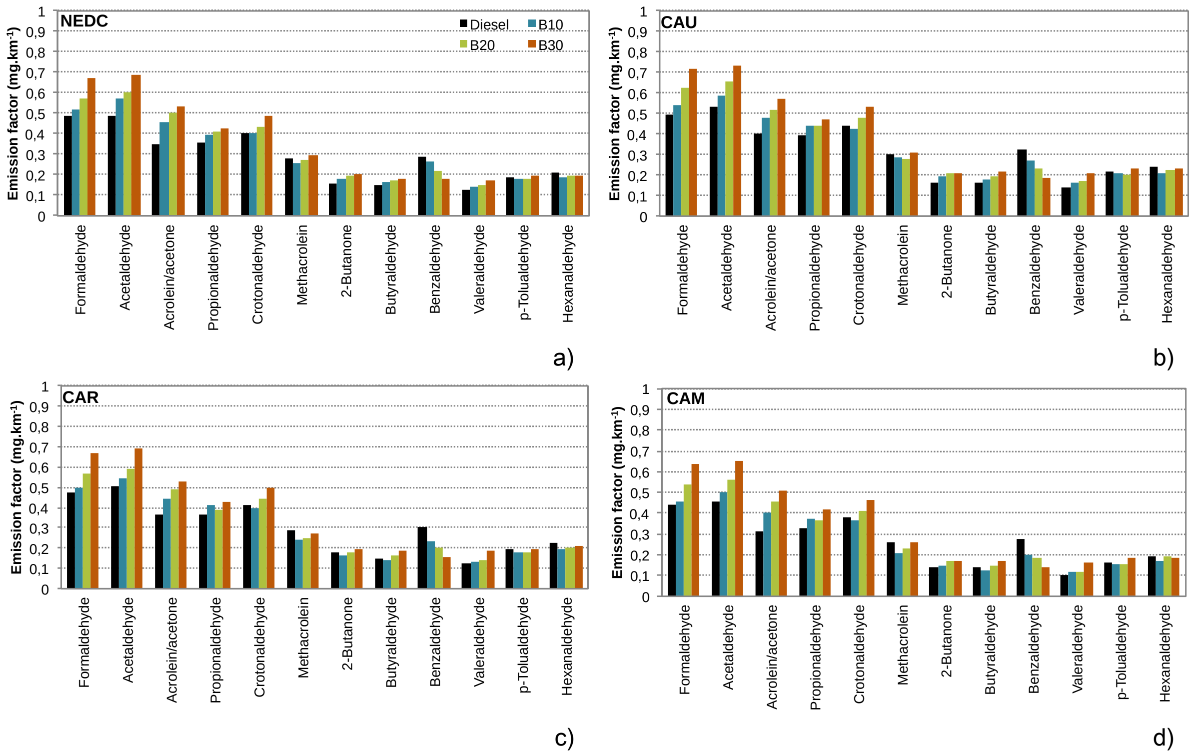


Figure 3.4 – Average of carbonyl compound emission factors (mg·km^{-1}) for diesel, B10, B20 and B30, over the a) NEDC, b) CAU, c) CAR and d) CAM driving cycles (from: Karavalakis et al., 2011b).

Formaldehyde, acetaldehyde and Acrolein/acetone are the aldehydes present in greater quantity in the exhaust gas when the diesel is used. Karavalakis et al. (2011b) verified that carbonyl compounds emissions are higher over the extra-urban cycle than over the urban cycle.

Additionally, subjects as aldehyde emissions other than formaldehyde, acetaldehyde, and acrolein, the effects of vehicle/engine age on carbonyl emissions, and ozone potential of carbonyl emissions, have been concerned in relation to exhaust emissions from biodiesel fuels. The importance of these concerns increases when more vehicles use biodiesel as a fuel and run over a long period of time (Peng et al., 2008). The aldehydes in exaust gases contribute to ozone formation in conjunction with NOx and sunlight (Macor et al., 2011). The Equivalent Ozone Production (EOP) is calculated based on the product of measured hydrocarbon emission factors and maximum incremental reactivity (MIR) (Carter, 1994; Chang et al., 2001; Peng et al., 2008). The MIR values for the carbonyl compounds presented in diesel and biodiesel blends are shown in Figure 3.5.

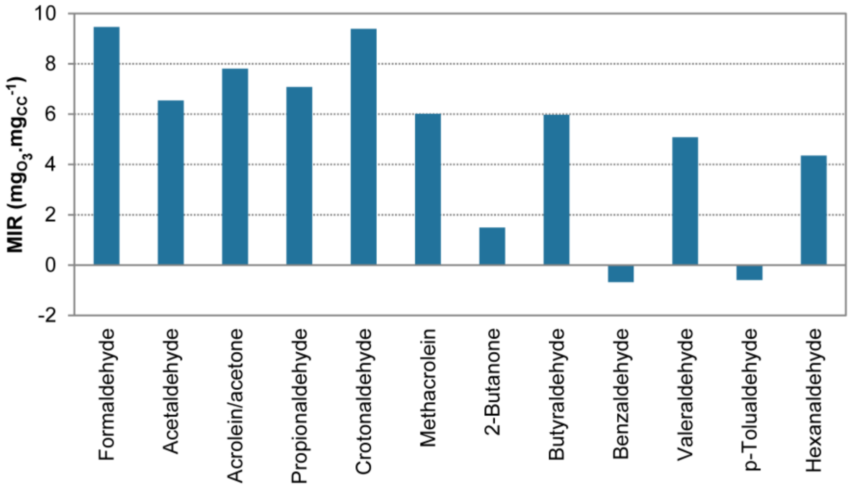


Figure 3.5 – Maximum incremental reactivity (MIR) of carbonyl compounds (CC) (Carter, 2009).

The main contributors to the Equivalent Ozone Production (EOP, Equation 3.1) are formaldehyde, crotonaldehyde, acetaldehyde, acrolein/cetone and propinaldehyde due to their high MIR and high concentrations in exhaust gases.

$$EOP = \sum_{i} (CCE_i \times MIR_i)$$

Equation 3.1
(Ballesteros et al., 2012)

Where:
EOP – Equivalent Ozone Production (mg O_3)
CCE – Carbonyl Compound Emission (mg CC)
MIR – Maximum Incremental Reactivity (mg O_3.mg CC^{-1})

3.1.5.2 Aromatic and PAH compounds

Aromatic and polyaromatic hydrocarbons (PAH) compounds, especially benzene, toluene and xylene (BTX) and derivate are toxic, mutagenic, carcinogenic and teratogenic and they contribute to the formation of tropospheric ozone (Krahl et al., 2002). As well as carbonyl compounds, the main sources of aromatic and PAH compounds are unburned molecules from fuel and structural modifications during combustion (Krahl et al., 2003; Turrio-Baldassarri et al., 2004; He et al., 2010). 85% of the published results (Figure 3.1) indicate that aromatic and PAH compounds emissions for biodiesel are reduced with regard to diesel. The reduction in PAH is usually due to enhanced adsorption of these components to PM (Turrio-Baldassarri et al., 2004). According to Cheung et al. (2009), Di et al. (2009), Krahl et al. (2003) and Takada et al. (2003), aromatic and PAH emissions are strongly dependent on the engine operating conditions (load, driving cycle, etc.).

The BTX compounds are most notably emitted by motor vehicles and they have been found in the urban areas air (Schauer et al., 2002). Nevertheless, no experimental results were found for BTX covering the usage of biodiesel blends over the NEDC or the CADC. However, Di et al. (2009) measured BTX emissions from a 4-cylinder direct-injection diesel engine. The experiments were performed at three engine loads corresponding to break mean effective pressure of 0.20, 0.38 and 0.55 MPa. The results obtained for diesel and B20 are compiled in Table 3.6.

Table 3.6 – Benzene, toluene and xylene emissions at various engine loads (Di et al., 2009).

$mg \cdot kW^{-1} \cdot h$		Diesel	B20	B40	B60	B80	B100
0.20 MPa	Benzene	79.2	109.1	127.6	143.0	133.3	119.3
	Toluene	17.1	5.8	6.2	5.4	3.6	3.3
	Xylene	69.7	20.4	25.4	24.5	13.4	12.8
	BTX	166.0	135.3	159.2	172.9	150.3	135.4
0.38 MPa	Benzene	57.0	59.4	75.1	83.7	76.4	76.2
	Toluene	8.3	4.5	3.8	3.8	2.6	2.5
	Xylene	33.2	13	16.1	12.7	10.1	8.3
	BTX	98.5	75.9	95	100.2	89.1	87
0.55 MPa	Benzene	28.1	28.5	33.1	38.3	39.2	35.4
	Toluene	3.3	1.9	2.0	1.9	1.6	1.4
	Xylene	18.7	7.5	8.4	7.7	6.2	5.6
	BTX	50.1	37.9	43.5	47.9	47	42.4

BTX emissions decrease with the increase of engine load due to BTX compounds are easily oxidized at high exhaust gas temperature, which typically occur at high engine loads (Takada et al., 2003; Di et al., 2009). On the other hand, the addition of biodiesel to diesel leads to the reduction of exhaust gas temperature, contributing to increase in the benzene emissions, especially at low engine load. It is also interesting to note that for biodiesel concentrations higher than 20%, the benzene emissions are higher that those for B20. This could be explained by the biggest temperature reduction from Diesel (510 K) and B20 (508 K) to B40 (502 K), B60 (501 K), B80 (501 K) and B100 (499 K) (Di et al., 2009). These temperatures are regarding the low engine load (0.20 MPa). However, the same trends were verified for the remaining engine loads.

Regarding toluene and xylene emissions, the results found by Di et al. (2009) reveal that those emissions are reduced with the addition of biodiesel mainly due to the oxygen enrichment that promotes the oxidation of these compounds.

3.1.6 Synthesis

The presence of oxygen on biodiesel fuels and their higher cetane number, in comparison to diesel, are important reasons pointed out to explain the reductions on PM, CO and HC emissions. Additionally, the low aromatic compound, the low carbon to hydrogen ratio and the advances in injection and combustion of biodiesel are factors arguing in favour of decreases on PM, CO and HC emissions, respectively. On the other hand, the majority of the experimental studies revealed that the oxygen content and the high cetane number of biodiesel contribute to the increase of the combustion temperature and therefore NOx emission will increase as well.

Regarding the CO_2 emissions, there are not consistent conclusions: some experimental results revealed that CO_2 emission are reduced when biodiesel is used instead of diesel as a result of low carbon to hydrocarbons ratio, while others studies indicate that CO_2 emissions increase or keep constant due to a more effective combustion.

85% of the published works showed that aromatic and PAH compound emissions for biodiesel reduce with regards to diesel, especially toluene and xylene, due to the oxygen content that improve the combustion efficiency, contributing to the degradation of these compounds. However, the decrease of exhaust gas temperature with the increase of biodiesel in the fuel blend is lead to the significant increasing of benzene emissions. The oxygen content is also pointed out as the cause of aldehyde emissions increasing, such as formaldehyde, acetaldehyde and acrolein. The increase of carbonyl compounds emissions when biodiesel is used is an issue of concern due to their ozone formation potential and their carcinogenic characteristics.

According to the majority of the studies consulted, it can be concluded that low biodiesel blends (< 30 %v/v) could be used to help in controlling air pollution and to reduce the pressure on scarce resources without compromising engine power and economy. Additionally, most of them also indicate B20 as the blend fuel with higher combustion efficiency and lower emissions than diesel and other blends.

3.2 Emissions characterization from EURO 5 diesel/biodiesel passenger vehicle[2]

Based on a set of diesel/biodiesel blends as fuel, some recent studies (Karavalakis et al., 2009, 2010, 2011b; Fontaras et al., 2010; Bakeas et al., 2011; Bermúdez et al., 2011; Randazzo and Sodré, 2011; Kousoulidou et al., 2012) have been published contributing to the understanding of the engine behaviour in terms of emission and performance profiles under specific driving cycles, such as NEDC and CADC (Figure 3.3). However, these studies focused on the EURO 2, EURO 3 and EURO 4 vehicle technology classes, thus referring to emission profiles of vehicles sold from 1996 to 2009.

Due to the identified lack of information on EURO 5 emission characterization, an experimental work was conducted to evaluate the effects of diesel/biodiesel blends on the fuel consumption and the gaseous emissions from a new diesel EURO 5 passenger vehicle. The vehicle used in this experiment was a Renault Megane 1.5 dCi (2011) equipped with a common-rail direct injection diesel engine and meeting EURO 5 emission standards. The technical specifications of the vehicle are listed in Table 3.7. This vehicle was selected because it is the most sold vehicle in Portugal with 7324 units sold between January and October 2011 (ACAP, 2010).

Table 3.7 - Technical specifications of the test vehicle.

Engine type	Renault Mégane 1.5 dCi
Fuel injection system	Direct injection, common-rail
Cylinders/valves	4/8
Displacement (cm^3)	1461
Maximum power (kW/hP)	81/110
Maximum torque (Nm)	240/1750 rpm
Weight (kg)	1215
Aerodynamic ($S(M^2)/Cd$)	2.21/0.326
Equipped with a DPF system	self-regenerating
Equipped with a EGR system	-

[2] Based on Lopes, M., Serrano, L., Ribeiro, I., Cascão, P., Pires, N., Rafael, S., Tarelho, L., Monteiro, A., Nunes, T., Evtyugina, M., Nielsen, O.J., Gameiro da Silva, M., Miranda, A.I., Borrego, C., 2014. Emissions characterization from EURO 5 diesel/biodiesel passenger car operating under the new European driving cycle. Atmos. Environ. 84, 339–348 (DOI: 10.1016/j.atmosenv.2013.11.071).

This vehicle, as all modern diesel cars, is equipped with diesel particulate filter systems in order to fulfil the requirements of EURO 5 standard. This vehicle is also fitted with an exhaust gas recirculation system.

Fuel blends containing 7%v/v (B7, the blend that is currently used in Portugal) and 20%v/v (B20) of soyabean/palm biodiesel (84%/16%), in volume basis, in petroleum-based diesel were tested and compared with a 100% diesel fuel (B0). The fuel properties are presented in Table 3.8.

Table 3.8 - Fuel properties used in the experiment.

Parameter/unit	B0	B7	B20	Test method
Density at 15 ºC ($kg \cdot m^{-3}$)	837.0	840.1	846.0	EN ISO 3675
Viscosity at 40 ºC ($mm^2 \cdot s^{-1}$)	2.430	2.845	2.980	EN ISO 3104
Flash point (ºC)	>55	74.5	76.5	EN ISO 2719
Water content ($mg \cdot kg^{-1}$)	<50	105	171	EN ISO 12937
Calculated cetane index	51.8	51.9	52.1	EN ISO 4264
FAME content [% (v/v)]	<0.1	6.9	20.0	EN 14078
Heating value ($MJ \cdot kg^{-1}$)	45.598	45.146	44.418	ASTM D-240
Distillation				
Recovered at 250ºC [% (v/v)]	36	34	27	EN ISO 3405
Recovered at 350ºC [% (v/v)]	93	93	93	EN ISO 3405
95% recovered (ºC)	361.6	359.5	357.1	EN ISO 3405

It is relevant to note the main differences when comparing biodiesel with fossil diesel: biodiesel is more viscous, fuel diesel has a higher heating value, biodiesel is denser and it has about 10-11% of oxygen content while petroleum-based diesel does not have oxygen. As discusses previously (section 3.1), these factors will influence the combustion process and, namely the fuel consumption and emission factors for gaseous and particulate pollutants.

The experiments were carried out with the vehicle placed over a chassis dynamometer (Figure 3.6), according to the NEDC (Figure 3.3), simulating the typical usage of a car in Europe in order to quantify vehicle emissions (CO_2, CO, NO_2, NO, SO_2, VOC and PM) under distinct driving conditions.

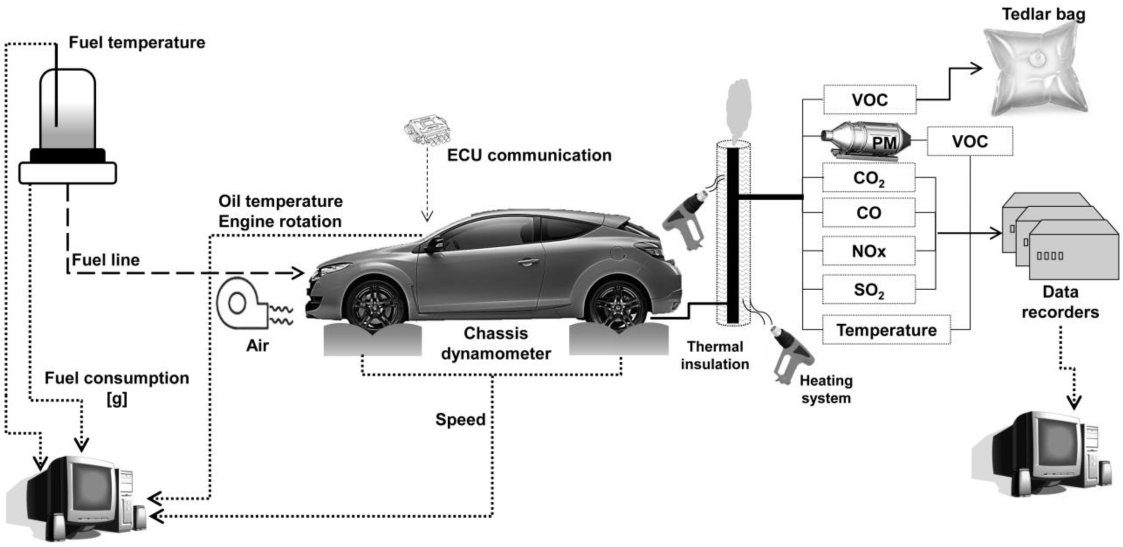


Figure 3.6 – Scheme of the experimental infrastructure.

To assure the comparability of the emission measurements, the NEDC was repeated four times for each fuel blend and each first replica was not considered in data analysis in order to minimize the impacts of the fuel change on the engine performance. Moreover, the exhaust gases and the engine coolant temperatures were approximately 100 ºC and 80 ºC, respectively, at the start of the test procedure, to guarantee that each trial was performed at the same conditions. Thus, the concentration measurements were performed under hot conditions.

3.2.1 Exhaust gas sampling and analysis

The sampling and analysis of regulated pollutant emissions from motor vehicles are performed in accordance to the European regulation (Directive 70/220/EEC and further amendments), following the constant volume sampling technique. This technique maintains a constant total flow rate of vehicle exhaust plus dilution air. With a constant volume sampling system, as exhaust flow increases, such as during heavy acceleration, the dilution air is automatically decreased and the sampling source is representative of exhaust variations.

The constant volume sampling method has been used to support vehicle emissions testing for over 25 years and the ‘bag’ measurement of emissions is the key method that is used for legislative purposes (Randazzo and Sodré, 2011). Bag measurements provide a single figure for CO, CO_2 and NOx emissions species for the complete drive cycle, but have their own limitations, providing no information on the emission profile throughout the test. Thus, a different sampling methodology based on continuous on-line exhaust gas composition measurements was adopted in the work presented here. This methodology provides a time profile for O_2, CO, CO_2, NOx, SO_2 and VOC along the experimental test of the vehicle.

For sampling the exhaust gas, an experimental apparatus was implemented, which allowed connecting the vehicle tail pipe to a larger duct simulating a flue gas stack chimney (Figure 3.6). The sampling probes and particulate matter filters were introduced in the vertical duct in a sampling hole. The location of the sampling section is in accordance with the Portuguese Standard 2167:2007. The entire system was heated above 100 ºC to prevent water vapour and organics condensation, avoiding any interference with the measurements. Moreover, a heated filter was installed in the sampling probe to remove particulate compounds, protecting the flame ionization detector that measures VOC.

The set of measured parameters and the respective equipment used in this experimental work is compiled in Table 3.9.

The monitoring of O_2, CO, CO_2, NO_2, NO, SO_2 and total VOC concentrations was carried out on-line and continuously (registering period: a second for O_2, CO, CO_2, NO_2, NO, SO_2 and a minute for total VOC). The gas sample was extracted and conducted to an infrared sensor to measure CO_2 concentration and to electrochemical cells through a heated line, for the remaining gaseous compounds. Regarding PM measurement, a parallel sampler extracted the exhaust gas and forces it to pass through an impactor, which separates particles according to their diameter. The particles have been divided into three fractions, corresponding to diameters above 10 μm (1st filter), between 2.5 μm and 10 μm (2nd filter) and less than 2.5 μm (3rd filter). The impactor which contained quartz filters was kept at the temperature of the system (above 100 ºC) to avoid condensation in the sampler pipe. The mass collected in the various filters was determined gravimetrically, after a drying process. After gravimetric determination, filter punches were analyzed by a thermo-optical transmission system in order to quantify the carbonaceous content into organic carbon and elemental carbon. Details of the analytical technique are provided in Alves et al. (2011). Finally, samples of exhausted gas were collected using Tedlar bags in order to perform VOC speciation analysis by gas chromatography according to the methodology described by Evtyugina et al. (2013).

Table 3.9 – Equipment used in the experimental work.

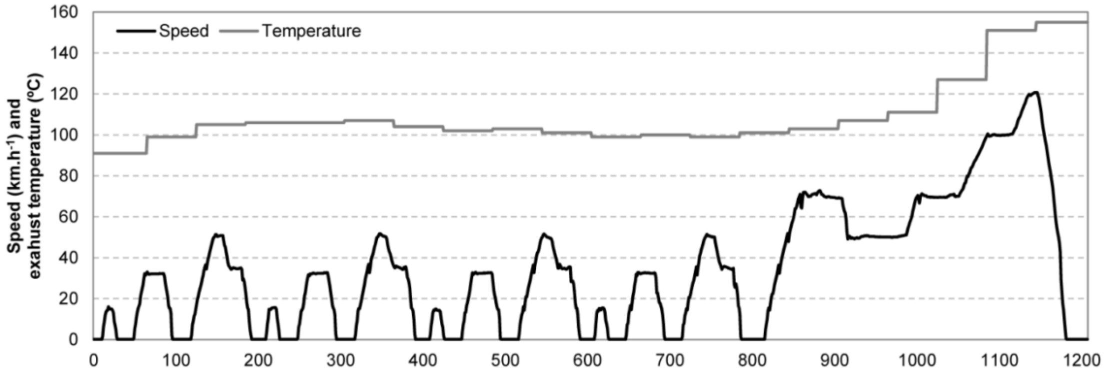
Equipment	Parameters	Detection limit	Response time (s)	Resolution	Accuracy	Test method
Andersen control unit	Dry gas meter	-	-	0.0001	< ± 2 % m.v.	-
Hot Box	Support and heating the filter sampling	-	-	-	-	ISO 23210:2009
Impactor and quartz filters	PM10 and PM2.5	-	-	-	-	ISO 23210:2009
Cold box	Bubblers cooling in an ice bath	-	-	-	-	EN 14790:2005
Thermocouple	Exhaust gas temperature	-	-	1	< ± 3	-
TESTO 350 XL (gas analyser)	O_2	0.1%	< 20	0.01 %	< 0.2 % m.v.	EN 15259:2007
	CO	1 ppm	< 40	1 ppm	< 5 % m.v.	
	CO_2	0.02 %	< 10	0.01 %	< 1.5 % m.v.	
	NO	1.8 ppm	< 30	1 ppm	< 10 % m.v.	
	NO_2	0.5 ppm	< 40	0.1 ppm	< 2 % m.v.	
	SO_2	1 ppm	< 30	1 ppm	< 5 % m.v.	
Bernath Atomic Model 3006 Analyser (flame ionization detector)	VOC	0.4 ppm	3	0.2 ppm	< 5 % Span	EN 15259:2007 EPA 25A
Balance Mettler (mod. AG285)	Mass	-	-	0.1 mg	± 0.017 mg	-
Balance Sartorius (PT 1200)	Mass	-	-	0.1 g	±0.058 g	
Gas chromatograph	VOC	0.4 ng	-		< ± 7 % m.v.	-
Thermo-optical transmission system	Elemental carbon / organic carbon	0.6 ppm(1)	1		± 2 · g·filter^{-1} (2)	-

m.v. - measured value

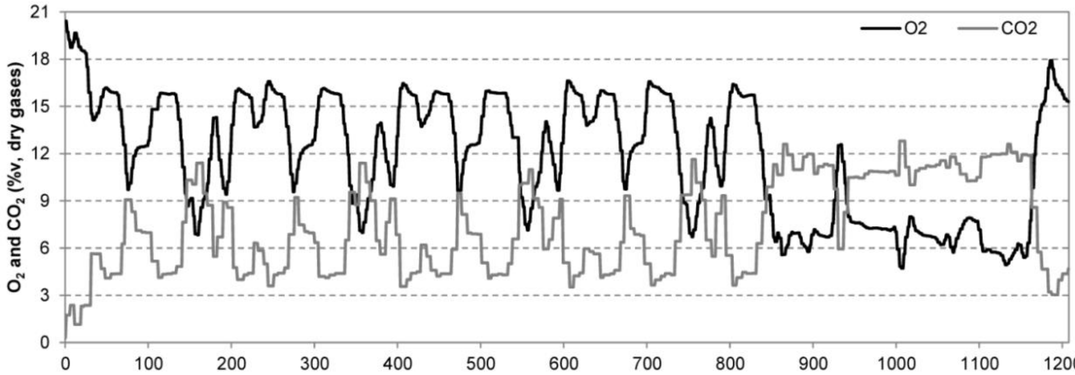
1 NDIR CO_2 analyzer

2 Accuracy based on TC variability on blank quartz filter

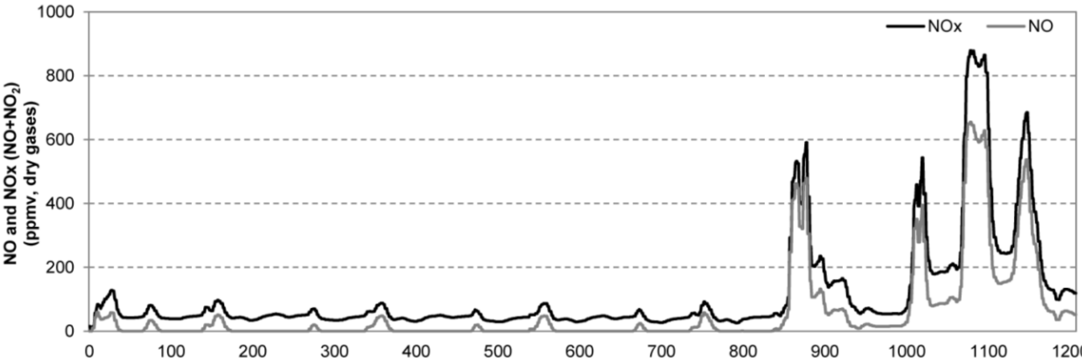
The measurement of concentration allows the understanding of the complete profile for O_2, CO, CO_2, NOx and SO_2. However, the equipments used have a time response (Table 3.9) which must be taken into account during the data post-processing. In spite of the equipments were capable to make the measurement cycle showing obvious variations of the various pollutants as a function of the speed in perfectly conditions, they took a little bit to take the first value when tests began. To address the time response problem, both speed and concentration curves were crossed in order to reject the first seconds of the concentration data series to coincide with the both curves. Since the concentration profiles from the tests were quite consistent, Figure 3.7 only represents the observed concentration profiles and the vehicle speed regarding the B20.



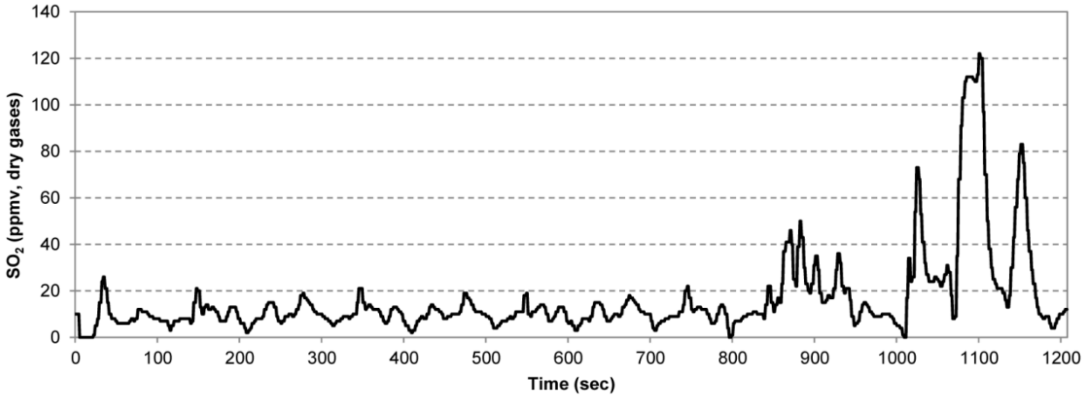
a)



b)



c)



d)

Figure 3.7 - B20 profiles of speed and exhausts gases temperature (a) and measured concentrations of O_2 and CO_2 (b), NOx (c) and SO_2 (d).

All trials followed the velocity profile that characterizes the NEDC cycle (Figure 3.7a), presenting a Pearson's correlation coefficient of 0.998. This value reveals a strong association between the standard and the experimental profiles, which allows the validation of the tests performed.

The O_2 and CO_2 contents vary oppositely throughout the test (Figure 3.7b). Moreover the observed CO concentrations are low, below the detection limit of the equipment (Table 3.9), which means that the combustion process is close to complete. Additionally, the analysis of the oxygen content shows the consistency of results, all tests varied in the range of 5.28 and 16.71 % of O_2, during the EUDC and UDC, respectively.

NOx (Figure 3.7c) and SO_2 (Figure 3.7d) concentrations were keeping at low levels during the UDC, increasing with both speed and exhaust gases temperature in the EUDC since both pollutants are produced especially at high temperatures (Lupiáñez et al., 2013; Shao et al., 2013). The concentration levels increase is especially observed during the speeding up periods and declines in cruise speed periods.

3.2.1 Determination of the mass and volumetric exhaust flow

The principle of mass conservation was applied to calculate of the mass and volumetric flow rate. The calculations were based on the assumption of complete oxidation of the chemical elements that compose the fuel and that the combustion air was dry. Furthermore, as the gaseous products resulting from combustion include a diversified set of substances, only their major components (CO_2, H_2O, O_2 and N_2) were considered for effects of global mass balance. In fact pollutants such as HC, H_2, CO, NO, NO_2, SO_2, HCl, HF, and some organic micropollutants (PAH, dioxins, furans, among others) have small effect on the total of exhaust emissions (Heywood, 1988).

Combustion flow was calculated by applying the principle of mass conservation, through the analysis of the chemical reactions translating the combustion processes of diesel (Equation 3.2) and biodiesel (Equation 3.3) fuels. The elemental composition of the fuels used in the experiments (%, m/m), on dry basis, was determined based on the analysis of the stoichiometry (Equation 3.2 and Equation 3.3). The data obtained are presented in Table 3.10.

$$C_{12}H_{26} + 18.5\ O_2 + 18.5 \times 3.76\ N_2 \rightarrow 12\ CO_2 + 13\ H_2O + 69.56\ N_2 \qquad \text{Equation 3.2}$$

$$C_{19}H_{34}O_2 + 26.5\ O_2 + 26.5 \times 3.76\ N_2 \rightarrow 19\ CO_2 + 17\ H_2O + 99.64\ N_2 \qquad \text{Equation 3.3}$$

Table 3.10 – Stoichiometric elemental composition (% m/m) of fuel, on dry basis.

Element	Elemental composition (%)	
	Diesel	Biodiesel
Carbon	5.314	5.799
Oxygen	21.848	22.381
Hydrogen	0.959	0.865
Nitrogen	71.879	70.956
Σ	100	100

Since the combustion process and its products are directly dependent of the existing air, it becomes indispensable to determine the current oxygen requirements, dependent of the stoichiometric requirement of oxygen that enables the complete oxidation of fuel. Thus, since the oxygen content of the combustion gases for each fuel type was measured, values of excess of air were arbitrated until the value of the current oxygen requirements is obtained (about 70%). Having compiled the information described, the mass flow of each combustion product ($\dot{m}_{gas\ i}$), expressed in $g_{gas\ i}\cdot h^{-1}$, was obtained by applying Equation 3.4.

$$\dot{m}_{gas\ i} = n_i \times M_i \times G_F \qquad \text{Equation 3.4}$$

Where, n_i is the elemental mass balance, in mol of element i by kg of dry fuel; M_i is the molar mass of product i, in $g\cdot mol^{-1}$; and G_F is the fuel consumption, in $g\cdot h^{-1}$.

Table 3.11 shows the fuel consumption and the mass air flow measured as indicator of the engine behaviour during the trials carried out, as well as the mass flow rates of exhaust gases determined according to the Equation 3.4. It should be noticed that the consumptions presented correspond to the mean value of the tests performed for each fuel, with the distinction between the respective driving cycles, whereby the flows obtained are presented as mean flows. By this way, the error associated with the experimental work was reduced. With the same purpose, the first test of each fuel type was excluded, to eliminate errors associated to the adjustment of the engine to the fuel.

Table 3.11 – Fuel consumption, mass air flow, and exhaust gas flow rates in mass and volume basis, by fuel and for each driving cycle.

Fuel type	Driving cycles	Fuel Consumption ($l\cdot100km^{-1}$)		Mass air flow ($kg\cdot h^{-1}$)	Exhaust mass flow ($kg\cdot h^{-1}$)	Exhaust volumetric flow ($Nm^3\cdot h^{-1}$)
		Range	Average			
B0	UDC	6.32 – 6.47	6.33	30.96	31.65	24.61
	EUDC	5.56 – 5.64	5.59	65.55	93.23	72.48
	NEDC	5.84 – 5.94	5.86	48.26	52.52	40.83
B7	UDC	6.35 – 6.48	6.44	32.22	32.35	25.14
	EUDC	5.56 – 5.67	5.61	64.78	94.36	73.34
	NEDC	5.89 – 5.97	5.92	48.50	53.37	41.48
B20	UDC	6.27 – 6.37	6.31	30.78	31.65	24.60
	EUDC	5.53 – 5.50	5.53	65.28	92.71	72.05
	NEDC	5.79 – 5.84	5.82	48.03	52.35	40.69

The fuel consumption and the mass air flow are similar among the different used fuel blends. Therefore there was no noticeable effect of the use of biodiesel in the diesel engine operation.

Once the mass flow of combustion products is obtained (Table 3.11), the determination of the volumetric flow rate was based on the estimation of the densities of each product (ρ_i, in $kg\cdot m^{-3}$) and assuming ideal conditions. The volumetric flow rates of exhaust (G_{exh}), in $Nm^3\cdot h^{-1}$, are also presented in Table 3.11.

3.2.2 Determination of the emission factors

The emission factors (EF) were calculated taking into account the volumetric flow rate for each fuel type analysed and each driving cycle (UDC and EUDC), the velocity (v) and the pollutant concentration emitted (C_{0i}), on a dry basis (as expressed by Equation 3.5). Emission factors were then obtained for each pollutant, for each driving cycle and for each fuel type examined, expressed in $g\cdot km^{-1}$.

$$EF = \frac{G_{exh} \times C_{0i}}{1000 \cdot V}$$ **Equation 3.5**

In order to establish the comparison between the different fuels analysed, mass concentrations were corrected for standard conditions. This condition of specific reference includes the temperature (T^0), the absolute pressure (P^0), and a value to molar fraction of oxygen (y_0^0), which depends on the applications (Portuguese Decree No. 178/2003). Since the Portuguese Decree No. 677/2009, of June 23, establishes the emission limit values applicable to combustion plants, especially on internal combustion engines, to an oxygen content of 15%, this was the value used in the correction of oxygen. The acronyms *T, P* and y_0 correspond, respectively, to the values of temperature, pressure and molar fraction of oxygen measured during the tests. In these circumstances the concentration in standard conditions, C_{0i}, expressed in mg.Nm^{-3}, was estimated through Equation 3.6.

$$C_{0i} = C_{mi} \times \frac{0.21 - y_0^0}{0.21 - y_0} \times \frac{T}{T^0} \times \frac{P^0}{P} \quad \text{Equation 3.6}$$

3.2.2.1 CO_2

One of the main motivations for the use of biodiesel in the transportation sector is the reduction of CO_2 emissions. Despite some authors (e.g. Xue et al., 2011) reporting a reduction of CO_2 emission when biodiesel is added to petroleum-based diesel, the current experimental results show that CO_2 emissions can slightly increase with the use of biodiesel blends (Figure 3.8). The same results were obtained by Bakeas et al. (2011), Fontaras et al. (2010) and Karavalakis et al. (2011).

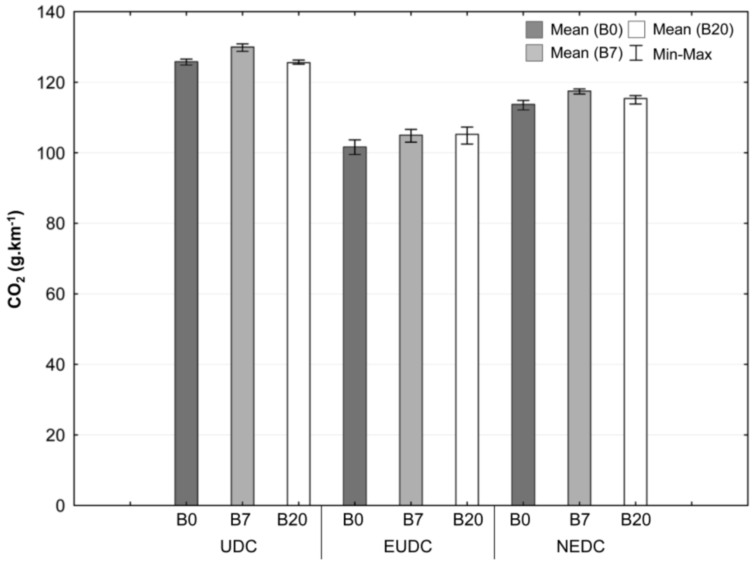


Figure 3.8 – CO_2 emission factors by fuel type and driving cycle.

Comparing the emission factors estimated for all tested fuel blends, B7 is the fuel with higher CO_2 emissions and higher fuel consumption (Table 3.11). On the other hand, B20 presents the lower fuel consumption, but the emission factors under the NEDC (115.36

g·km^{-1}) are between pure diesel (113.71 g·km^{-1}) and B7 blend (117.48 g·km^{-1}). These two factors could probably mean that the B20 blend leads to a more efficient and complete combustion than B0 and B7.

3.2.2.2 CO

As indicated in Table 3.9, the detection limit of the equipment used (TESTO 350XL) is 1 ppm and the accuracy error of the analyser is 5% of the value measured. The high values measured were founded for B7, nevertheless the CO concentrations in the exhaust gas were within or below the detection level of the monitoring equipment used. Taking this into account, it was not possible to conclude about CO emission behaviour using B0, B7 and B20 fuels.

3.2.2.3 NOx

Various nitrogen-based components are formed during the combustion process on a diesel engine, in particular NO and NO_2. The formation of NOx depends mainly on the oxygen available, the local combustion temperatures and the load conditions (Sun et al., 2010). The nitrogen oxides emission factors obtained by fuel type and driving cycle are presented in Figure 3.9.

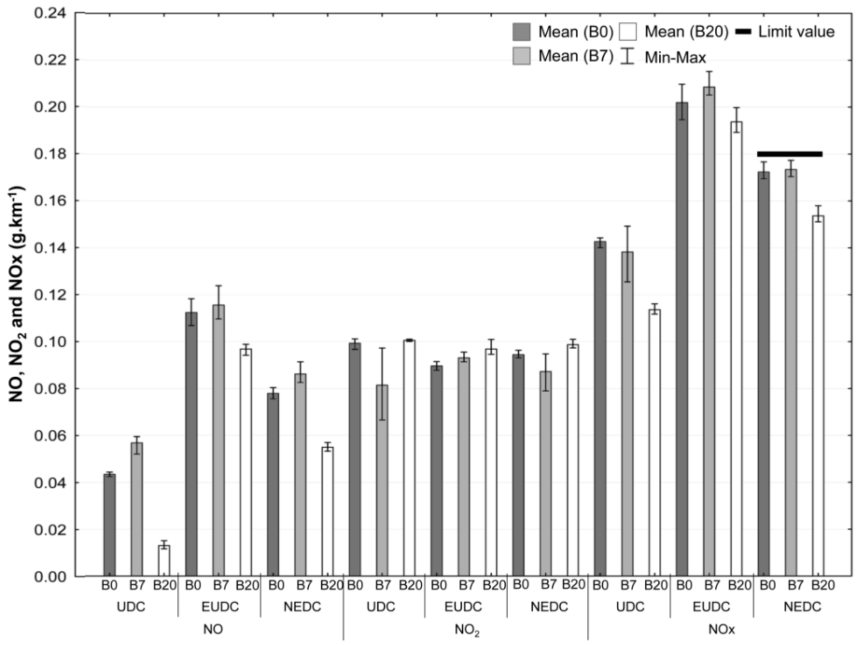


Figure 3.9 – NO, NO_2 and NOx (NO+NO_2) emission factors by fuel type and driving cycle, and the emission limit value indicated by the EC Regulation 715/2007.

Looking at the complete driving cycle, the NOx emissions are below the EURO 5 limit value for all blends (0.18 g·km^{-1}, EC Regulation 715/2007). Typically, the NOx produced by a combustion reaction on a diesel engine is about 98% NO (Sun et al., 2010). However, the experimental results point out a distribution of about 50% of NO and 50% of NO_2, which means that the combustion processes occurred in the presence of excessive O_2, allowing the oxidation of NO to NO_2 from the motor to the tailpipe.

B20 was the fuel with lower NOx emission factors (0.15 g·km^{-1} over NEDC) with a reduction of 10.8% and 11.4%, when compared to B0 and B7, respectively. Furthermore, the trend of NO emissions for each fuel is similar to NOx. This can be explained by the reduced need of air and fuel (see Table 3.11) of B20, since NO is mainly formed during the combustion process, in other words, B20 promotes a more efficient combustion (as already mentioned in section 3.2.2.1).

The exhaust gas temperatures of B20 and B0 are similar (109.1 ºC and 109.0 ºC for B0 and B20, respectively) and higher than B7 (100.4 ºC), which could explain the lower NO_2 emissions associated to B7 over UDC and NEDC, due to NO_2 being mainly formed by the Zeldovich mechanism (Lavoie et al., 1970).

Besides the results not displaying a clear trend, they point out to a decrease of NOx emissions, mainly due to the increase of combustion efficiency with higher mixture rates of biodiesel. The improvement of combustion efficiency is probably due to the increase of the blend's viscosity (biodiesel is more viscous than diesel – see Table 3.8), which can play an important role in improving the lubrication of the injection metallic components of the engine.

3.2.2.4 SO_2

The SO_2 present in exhaust gas is entirely due to the sulphur content of the fuel. As Table 3.8 shows, the fuels used in these set of tests had higher sulphur content than the maximum allowed in Europe (10 ppm) by EN 590:2009. In this sense, the SO_2 emission factor obtained should be just analysed as variations between B7 and B20 regarding pure diesel (Figure 3.10).

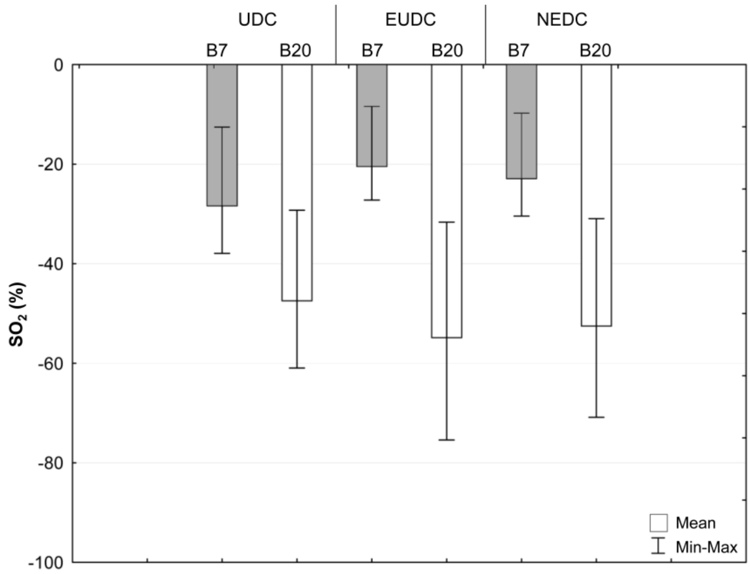


Figure 3.10 – Variation on SO_2 emission factor by fuel type and driving cycle, relative to pure diesel.

Figure 3.10 confirms the positive influence of the use of biodiesel blended in diesel. The obtained results show a reduction on SO_2 emission factor compared with pure diesel, in more than 20% using B7 and more that 50% using B20, over the UDC, EUDC and NEDC.

3.2.2.5 Particulate matter

According to the majority of the studies regarding the impact of biodiesel on particulate matter emissions (e.g. Bakeas et al., 2011; Xue et al., 2011), the use of a biodiesel blend causes a reduction in PM emissions. However, these studies refer to vehicles with previous technology than the vehicle tested (EURO 5). As described at the beginning of the section 3.2, the EURO 5 vehicles are equipped with diesel particulate filter a system, which means that PM emissions can be reduced in 90% (Bergmann et al., 2009; Tente et al., 2011). Taking this into consideration, the same filters were used in the four replicas of each fuel blend in an attempt to sample as much particulate matter mass as possible. After, the filters were weighed in laboratory, but the mass of the accumulated particulate matter in the filters was below the detection limit and no conclusion could be taken concerning the PM emissions with the use of the different biodiesel blends. Diesel particulate filter are not only effective in removing larger particulate matter such as PM10, but also effective in removing smaller particulate matter because all size fractions were removed by this filters. This finding confirms that diesel particulate filter installed in modern diesel light vehicles are in fact highly efficient and emissions cannot be quantified by gravimetric methods. Thus, this methodology is inappropriate to quantify PM emissions in vehicles equipped with diesel particulate filters.

Despite the low content of particles found in the filters, it was possible to quantify the levels of total particulate carbon (Figure 3.11) using a thermo-optical transmission system, including its speciation in organic carbon (OC) and elemental carbon (EC) for fine particulate fractions (PM<2.5).

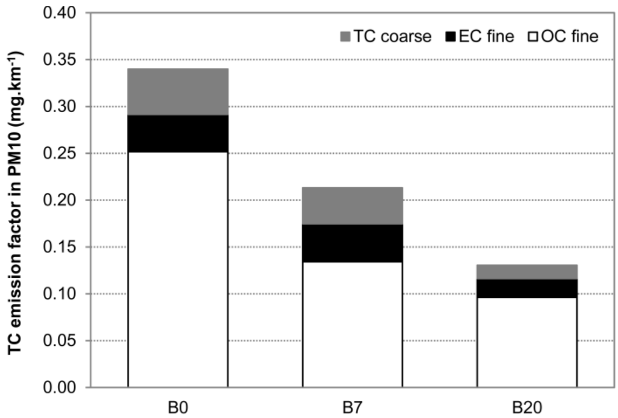
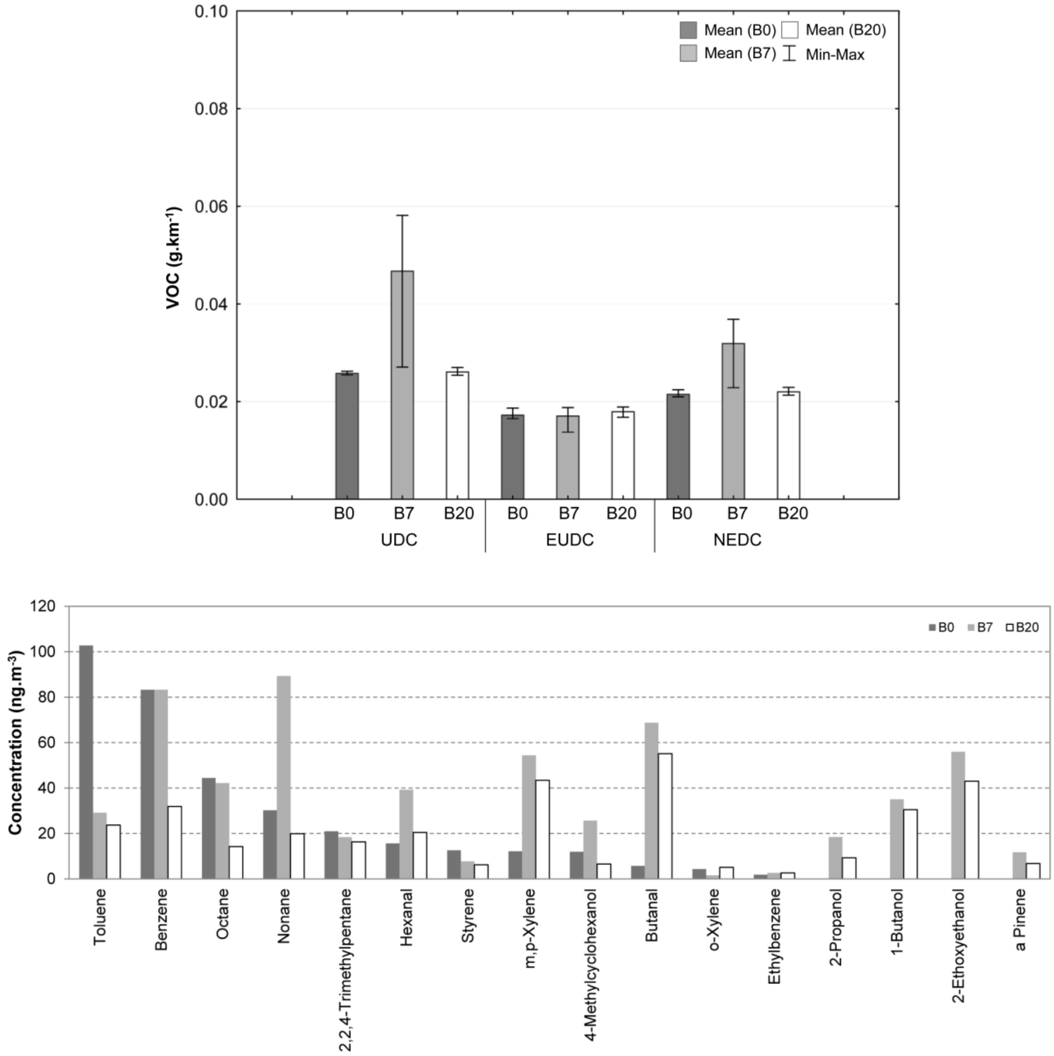


Figure 3.11 – Coarse and fine fraction (EC and OC) of total carbon (TC) emission factor in PM10, for B0, B7 and B20, considering all the NEDC.

The main carbonaceous content was concentrated in the fine fraction of all experiments, and is dominated by organic compounds, The OC/EC ratio ranged between 3 and 6 in the fine fraction. A decrease in emission factor for total carbon is observed with an increase of biofuel in the blend mixture. The emission factor of total particulate carbon could be used as a lower limit of PM emission factor for these experiments.

3.2.2.6 VOC

As described in section 3.2.1, two different tupes of measurements of VOC concentrations took place during the experiments: (1) through the flame ionization detector total VOC concentrations were measured per minute; and (2) a sample of exhausted gases was collected into a bag during the third UDC and EUDC of each NEDC in order to perform a VOC speciation analysis by gas chromatography. Figure 3.12a represents the total VOC emissions from the three fuels used, and Figure 3.12b shows the concentration of a set of VOC species found in the exhaust gas.



a)

b)

Figure 3.12 – Total VOC emission factor (a), and concentration of some species of VOC, for B0, B7 and B20 (b).

Compared with pure diesel, the B7 fuel displays higher values of total VOC emissions (Figure 3.12a), especially over the UDC, while the B20 fuel presents similar values to B0. However, the comparison between B7 and B20 fuels indicates that total VOC emissions decrease with higher biodiesel rates. Lower emissions may result from higher cetane number and oxygen content for B20 fuels. Fuels with high cetane number can reduce ignition delay and help promote more complete combustion, which could lead to the reduction of hydrocarbon emissions. In addition, higher oxygen content in B20 fuel helps to combust completely and reduces emissions (Peng et al., 2008; Rounce et al., 2012).

Gas chromatography results (Figure 3.12b) show that the set of VOC species and their concentrations change according to the fuel blend used. Sixteen different VOC species were found in B7 and B20, instead of the twelve presented on exhaust gases from experiments with pure diesel. The set of dominant VOC (species with concentration above 50 $ng \cdot m^{-3}$) regarding pure diesel is characterized by the presence of benzene (25.9%), toluene (21.1%) and octane (18.1%). On the other hand the set of dominant VOC for B7 includes nonane (16.0%), benzene (13.7%), butanal (11.1%), m,p-xylene (10.6%) and 2-ethoxyethanol (8.9%). Finally, for B20 the main VOC are butanal (18.3%) and m,p-xylene (14.1%). The obtained results point out that the concentration of the three main VOC species in exhaust gases from B0 (benzene, toluene and octane) decrease between 60 and 80% if a B20 blend is used.

It is also interesting to verify that specific VOC species may appear in exhaust gases if a biodiesel blend is used as fuel instead of pure diesel, namely 2-propanol, 1-butanol, 2-ethoxyethanol, α-pinene.

In accordance to Peng et al. (2012) the dominant VOC of pure diesel engine exhausts have higher chronic hazard quotients and hazard indices than VOC from B20. Thus, the use of pure diesel is more injurious for human health than biodiesel blends, in terms of VOC emissions.

3.2.3 Synthesis

The influence of diesel/biodiesel blends on the fuel consumption and the exhaust gas emissions patterns of a EURO 5 passenger vehicle (technology from 2009 to 2014) was assessed. Experiments were performed using a Renault Megane 1.5 dCi (2011), operated over the New European Driving Cycle (NEDC) on a laboratory chassis dynamometer. Fuel blends containing, in volume basis, 7% (B7) and 20% (B20) of biodiesel (84% soybean / 16% palm) in petroleum-based diesel were tested and compared with a 100% diesel fuel (B0).

Despite the reduction of CO_2 emissions as one main reason for the use of biodiesel in road transportation, the results of this experimental work show that CO_2 emissions may slightly increase with both biodiesel blends (B7 and B20), may be due to a more efficient combustion revealed.

The analysis of NOx within the set of fuels tested allows the confirmation that B20 was the better blend in terms of emissions and also combustion efficiency. The opposite was found with B7. In the combustion chamber, the NO emissions decrease in the presence of B20, when compared to B0. On the other hand, after the combustion, NO_2 emissions increase with B20 and decrease with B7. This occurred mainly because B20 allows higher combustion temperature (due to a better efficiency) than B7 and B0.

The results show a positive influence of the use of biodiesel blended in diesel in the SO_2 emissions. Regarding the complete NECD is possible to reduce SO_2 emission factor from pure diesel in more than 20% using B7 and 50% using B20. On the other hand, the results were inconclusive concerning the influence of biodiesel on PM emissions, since the mass collected in the filters (by gravimetric method) was below the detection limit. However, through a thermo-optical transmission system, it was possible to quantify the levels of both organic and elemental carbon for PM2.5, which allowed verifying that, for all the experiments, the main carbonaceous content was concentrated in the fine fraction and is dominated by organic compounds. Additionally, the total carbon emissions decrease with the increasing of biodiesel content in the blend.

Total VOC emissions may increase with biodiesel blend ratios. However the set of VOC species present on exhausted gases is highly dependent on the fuel blend used.

B7 had a non-expectable behaviour regarding all the parameters that were taken into account. For all the studied pollutants and for all the replicas executed, large error bar for B7 were obtained. Probably, the variation on the temperature of exhausted gases founded to B7 (100ºC by average) in relation to B0 and B20 (109ºC by average) may indicates that the combustion temperature was lower for B7 than for other blends and then justify the odd behaviour of B7. Moreover, the higher fuel consumption and the mass air flow, as well as high CO_2 and VOC emissions and lower NOx emissions for B7, point out to the same direction. To sum up, lower combustion temperature that may occur at B7 probably destabilized the combustion and catalyst processes and thus increasing the fuel consumption and CO_2, CO, NOx and VOC emissions.

Chapter 4. Emission scenarios

To assess the impact of biodiesel use on road transport sector emissions, two study domains were considered: Portugal and the Porto urban area. For both domains two emission scenarios were built:

1. **The reference scenario (REF)** considering that biodiesel is not used as fuel by road transport sector;
2. **The B20 scenario (B20)** assuming that all diesel engines are fuelled with diesel blended with 20% of biodiesel.

Atmospheric pollutant emissions for the REF scenarios were estimated using the TRansport Emission Model for line sources (TREM, Borrego et al., 2003). The emission factors identified and discussed on Chapter 3 regarding the use of B20 fuel were used to correct the emissions of REF to obtain the B20 scenario.

4.1 TRansport Emission Model for line sources (TREM)

The TRansport Emission Model for line sources (TREM), was firstly developed on the basis of MEET/COST methodology and focused on regulated pollutants (CO, NOx, VOC, CO_2, SO_2 and PM10) (Borrego et al., 2000, 2003, 2004; Tchepel, 2003). Recently, the TREM Hazardous Air Pollutant (TREM-HAP) extension was developed to calculate emissions of benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, naphthalene and PM2.5 (Tchepel et al., 2012).

The main objective of the TREM is the estimation of road traffic emissions with high spatial resolution, which can be used as supporting tool for air quality modelling studies and air quality management proposes. TREM considers roads as line sources and emissions induced by vehicles are estimated individually for each road segment considering detailed information on traffic fluxes, vehicle fleet distribution and road segment length (Figure 4.1).

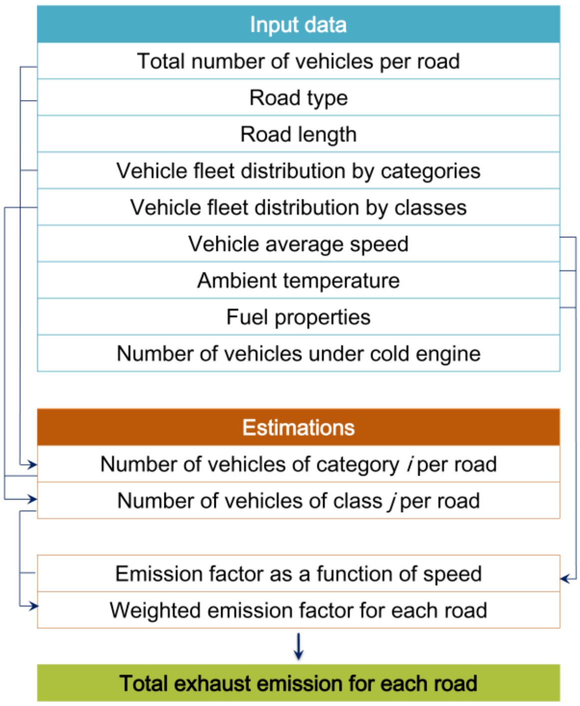


Figure 4.1 - TREM input data and main calculation modules for exhaust emission quantification (adapted from Tchepel, 2003).

TREM uses the state of the art emission factors from the EMEP/EEA air pollutant emission inventory guidebook (EMEP/EEA, 2013) for regulated pollutants, and updated emission factors from Artemis methodology (André and Joumard, 2005; Boulter and McCrae, 2007) for hazardous air pollutant relevant for mobile source. The emission factors are function of the average speed and vehicle class (based on engine age, type, and capacity, vehicle weight, fuel type, and emission reduction technology). To process these data, TREM is linked to Geographical Information System (ArcGIS) (Tchepel, 2003; Tchepel et al., 2012).

In sum, three types of input data are needed for TREM application:

- The vehicle fleet distribution;
- The road network of the study area, including the type and the length of each road;
- Traffic information of each road (traffic fluxes and average speed of circulation).

Based on the national statistics on automobile sector for 2009 (ACAP, 2010), it was possible to characterize the national vehicle fleet by age and type (Table 4.1). The vehicle types considered are: light passenger vehicles (LPV), light duty vehicles (LDV), heavy passenger vehicles (HPV) and heavy duty vehicles (HDV).

Table 4.1 – Portuguese vehicle fleet by age and type in 2009 (ACAP, 2010).

Age (year)	LPV	LDV	HPV	HDV
		(%)		
< 1	5.52	3.93	4.03	4.64
1 – 2	4.08	3.32	3.96	4.34
2 – 3	5.74	4.70	5.40	5.96
3 – 4	5.58	5.60	4.83	5.87
4 – 5	5.35	5.38	4.02	5.35
5 – 10	26.79	30.59	22.21	20.48
10 – 15	27.67	29.39	21.38	19.17
15 – 20	15.32	13.06	11.97	12.10
>20	3.95	4.03	22.20	22.09

Due to the lack of detailed information regarding the number of existing vehicles by type of fuel, the characterization of the vehicle fleet distribution is based on the number vehicles sold in 2009 by fuel type (ACAP, 2010). The vehicle fleet distribution estimated per vehicle type and fuel is presented in Figure 4.2.

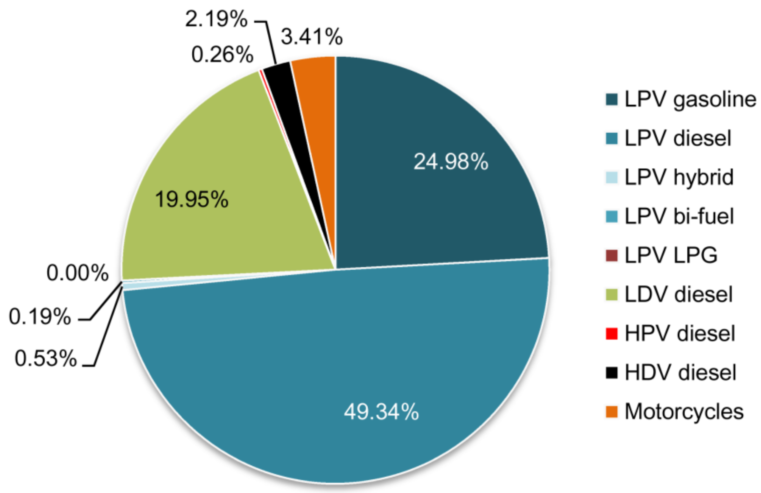


Figure 4.2 – Vehicle fleet distribution by type and fuel.

According to the Figure 4.2, almost 72% of the vehicle fleet is diesel fuelled and the quantity of HPV, LDV and HDV fuelled by other fuel than diesel is negligible. Regarding LPV, 32.52%, 66.50%, 0.71% and 0.26% are fuelled by gasoline, diesel, hybrid and gasoline/liquefied petroleum gas (LPG), respectively.

The available information to characterize the national road network in terms of traffic volume only regards to motorways, which is not enough to calculate the total emissions from the road transport sector over Portugal. This problem was overcome applying the TREM-HAP model over the Northern Region of Portugal, for which the available information is significantly more detailed. It includes the mean daily traffic for several roads of the Northern Region of Portugal, namely: motorways, other major roads, secondary roads and urban roads over the municipality of Porto (Figure 4.3) (Borrego et al., 2009).

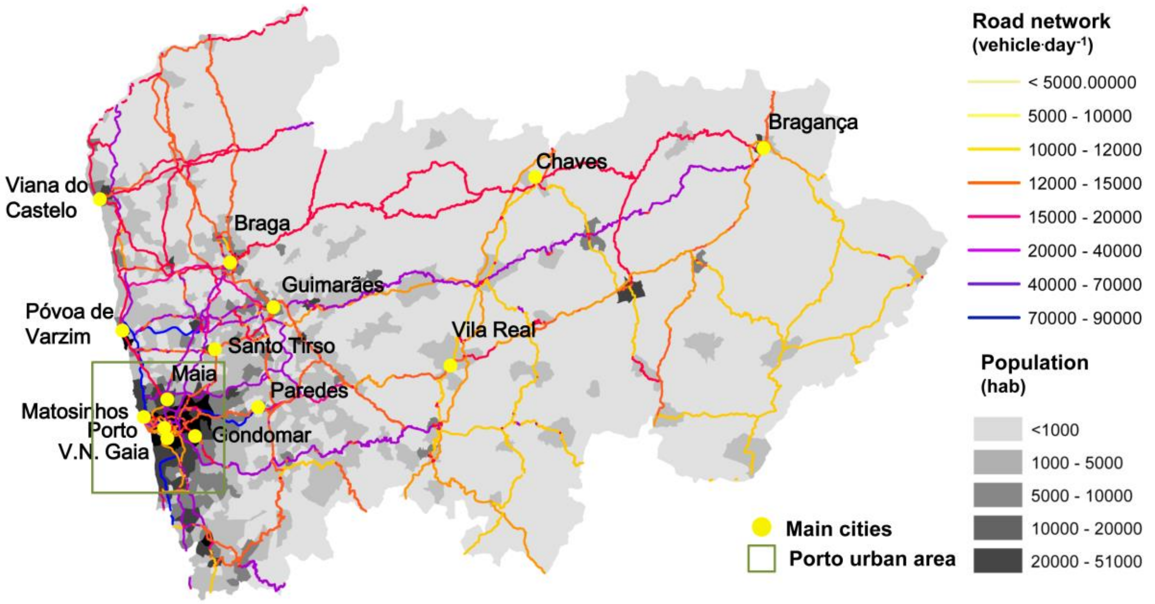


Figure 4.3 – The TREM-HAP simulation domain covering the Northern region of Portugal: the Porto urban area, the road network and the daily mean traffic volume (vehicle·day^{-1}) for each road, main cities and population distribution.

TREM-HAP was applied over the Northern region of Portugal (Figure 4.3): a first run to calculate the emissions from gasoline vehicles and another one considering diesel vehicles. TREM-HAP calculate the mass of CO, CO_2, PM10, NOx, NMVOC, acetaldehyde, acrolein, formaldehyde and PM2.5 emitted ($g_{pollutant}.km^{-1}$), as well as the mass of fuel consumed ($g_{fuel}.km^{-1}$) for each road. The average emission factors ($g_{pollutant}.g_{fuel}^{-1}$) were calculated for each road of the Northern region of Portugal (Table 4.2).

Table 4.2 – Average emission factors ($g_{pollutant}.g_{fuel}^{-1}$) calculated by TREM and TREM-HAP for the Northern region of Portugal.

	$g_{pollutant}.g_{fuel}^{-1}$	
Pollutant	Diesel	Gasoline
NOx	2.05E-02	8.93E-04
PM10	6.56E-04	1.90E-05
PM2.5	1.27E-03	7.75E-05
CO	4.99E-03	5.61E-03
NMVOC	1.63E-03	4.07E-03
Formaldehyde	1.23E-04	6.09E-05
Acethaldehyde	6.69E-05	2.69E-05
Acrolein	3.08E-05	6.79E-06
Benzene	9.51E-06	2.01E-04
CO_2	3.14E+00	2.85E+00

4.2 The REF scenario

The reference scenario (REF) considers that the diesel used by the road transport sector is a petroleum-based diesel, meaning that no biodiesel is used.

From the information provided by TREM-HAP and to determine the road traffic emissions for Portugal, the average emission factors for each pollutant and fuel (Table 4.2) were multiplied by the quantity of fuel sold (diesel and sum of gasoline 95 and 98) in Portugal during 2012, at municipality scale (URL 10) (Figure 4.4).

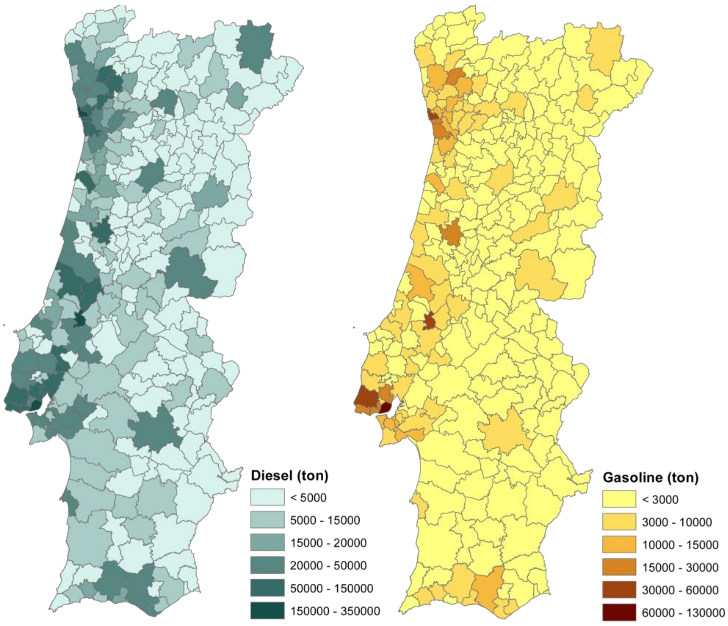


Figure 4.4 – Diesel and gasoline (95+98) sold by municipality in 2012 (URL 10).

Since the TREM-HAP simulation (Figure 4.3) covered the entire Porto urban area (Figure 4.5), the fuel consumption data was not taken into account, but the road network and the daily mean traffic volume for this area. Keeping the road transport emissions over the roads instead of distributed by municipality areas is especially important for the Porto urban area to improve the emission information to further air quality simulation (Chapter 6).

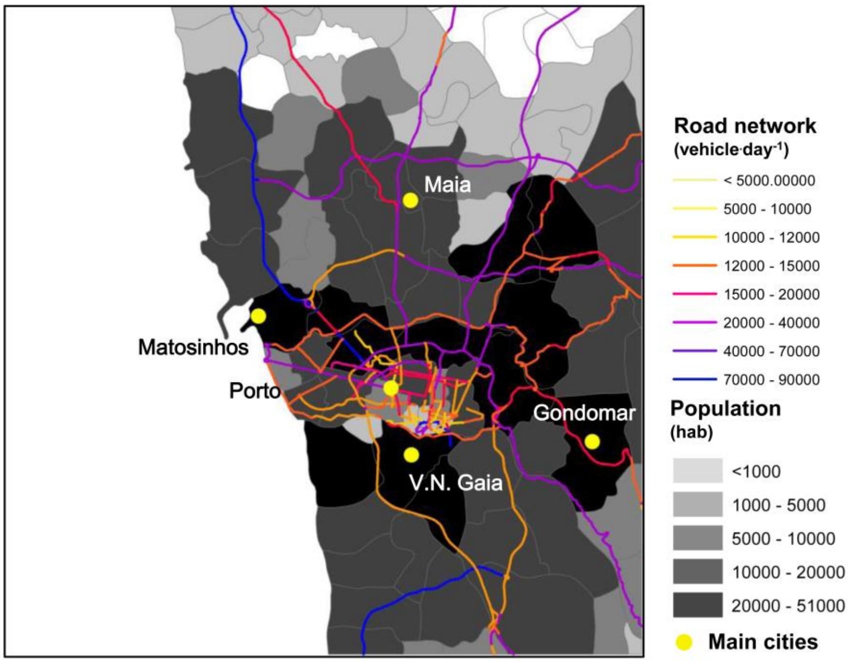


Figure 4.5 – The Porto urban area domain: population distribution, main cities and road network including the daily mean traffic volume (vehicle·day^{-1}).

Road-transport emissions estimated by TREM-HAP for mainland Portugal and the Porto urban area are compiled in Table 4.3. Because this is the reference scenario, atmospheric pollutant emission from TREM-HAP were compared against the road transport emission on national emission inventory (APA, 2011). Additionally, they are compared to INERPA emissions, which do not consider the use of biodiesel blends for road transports to emission estimation, in order to validate the methodology here used and to build REF scenarios with more realistic emission values. The representativity of the Porto urban area in terms of road-transport emissions within Portugal is also shown in Table 4.3.

Table 4.3 – Road-transport sector annual pollutant emissions estimated by TREM-HAP (T), regarding the REF scenario, and included in INERPA (I), over mainland Portugal and the Porto urban area. Ratio of emission estimated and INERPA emissions (T/I) and the representativity of the Porto urban area in mainland Portugal's emissions (Porto/Portugal).

Pollutant	Mainland Portugal TREM-HAP (T)	Mainland Portugal INERPA (I)	Mainland Portugal T/I (%)	Porto urban area TREM-HAP (T)	Porto urban area INERPA (I)	Porto urban area T/I (%)	Porto/Portugal (%)
Acroleine	129.8	-	-	23.1	-	-	17.8
Benzene	252.2	-	-	36.7	-	-	14.5
Acetaldehyde	295.2	-	-	45.4	-	-	15.4
Formaldehyde	556.9	-	-	85.5	-	-	15.3
PM2.5	2478.1	5136.9	48.2	357.3	356.064	100.3%	14.4
PM10	2636.3	5326.7	49.5	397	370.9	107.0%	15.1
NMVOC	10854.8	20889.9	52.0	2082	2648.1	78.6%	19.2
CO	25878.3	130253	19.9	7483.5	13605.7	55.0%	28.9
NOx	82616.2	99917.8	82.7	5641	5684.2	99.2%	6.8
CO_2	15570067.6	17441509.0	89.3	1223253.4	1205696.3	101.5%	7.7

The comparison between the emissions determined through TREM-HAP and emission in the INERPA (Table 4.3) revealed that the methodology presented here based on fuel consumption was able to estimate more than 80% of the total NOx and CO_2 emissions for mainland Portugal, but only about 20% of CO and 50% of NMVOC, PM10 and PM2.5 emissions. Different results were found for the Porto urban area, mainly because the methodologies used for each case study were somewhat different. The comparison between TREM-HAP and INERPA emissions suggest that TREM-HAP was able to estimate emissions with more accuracy based on road-network and vehicle fleet information that using national statistics on fuel consumption, as expected. The pollutant with worst result was CO, for which the TREM-HAP was able to estimate only half of its emissions, while slightly overstates PM10, PM2.5 and CO_2 emissions. NMVOC and NOx emissions estimated by TREM-HAP corresponding to about 80% and 99% of their INERPA emissions. These variations on emission estimations are mainly derived from the models used with in this work and INERPA: the COPERT IV (Ntziachristos et al., 2009) emission model is used within INERPA, while road-transport emissions were estimated by TREM in this work. The extrapolation made from the Northern Region of Portugal as well as the non-consideration of cold-emission, due to the lack of information on origin/destiny matrix per municipality, are also factors that contributed to the verified differences, especially on total NMVOC, PM10 and CO emissions. INERPA does not include emissions of acroleine, benzene, acetaldehyde and formaldehyde; and no other emission inventory that included these pollutants was found for Portugal.

The differentials between emissions from TREM-HAP and from the national inventory were determined and applied to correct REF scenario. As it will be discussed in next section, the same differentials were also applied to correct the B20 emission scenario.

As an example of the emission distribution for both case studies, Figure 4.6 presents the REF emissions of NOx (Figure 4.6a,c) and formaldehyde (Figure 4.6b,d), since they are the most important pollutants emitted by the road transport sector from each pollutant group (regulated and non-regulated pollutants), according to Ho et al. (2007) and APA (2014). In Figure 4.6, NOx and formaldehyde emissions are in tons per year for each municipality of Portugal, while for the Porto urban area there was a need to convert line emission (from TREM-HAP) to emissions in area in order to perform the emission correction (see the previous two paragraphs). Both emission correction and the representation were made based on a $1\times1km^2$ grid to be compatible with the horizontal resolution of the air quality simulation domain (topic addressed further in Chapter 5).

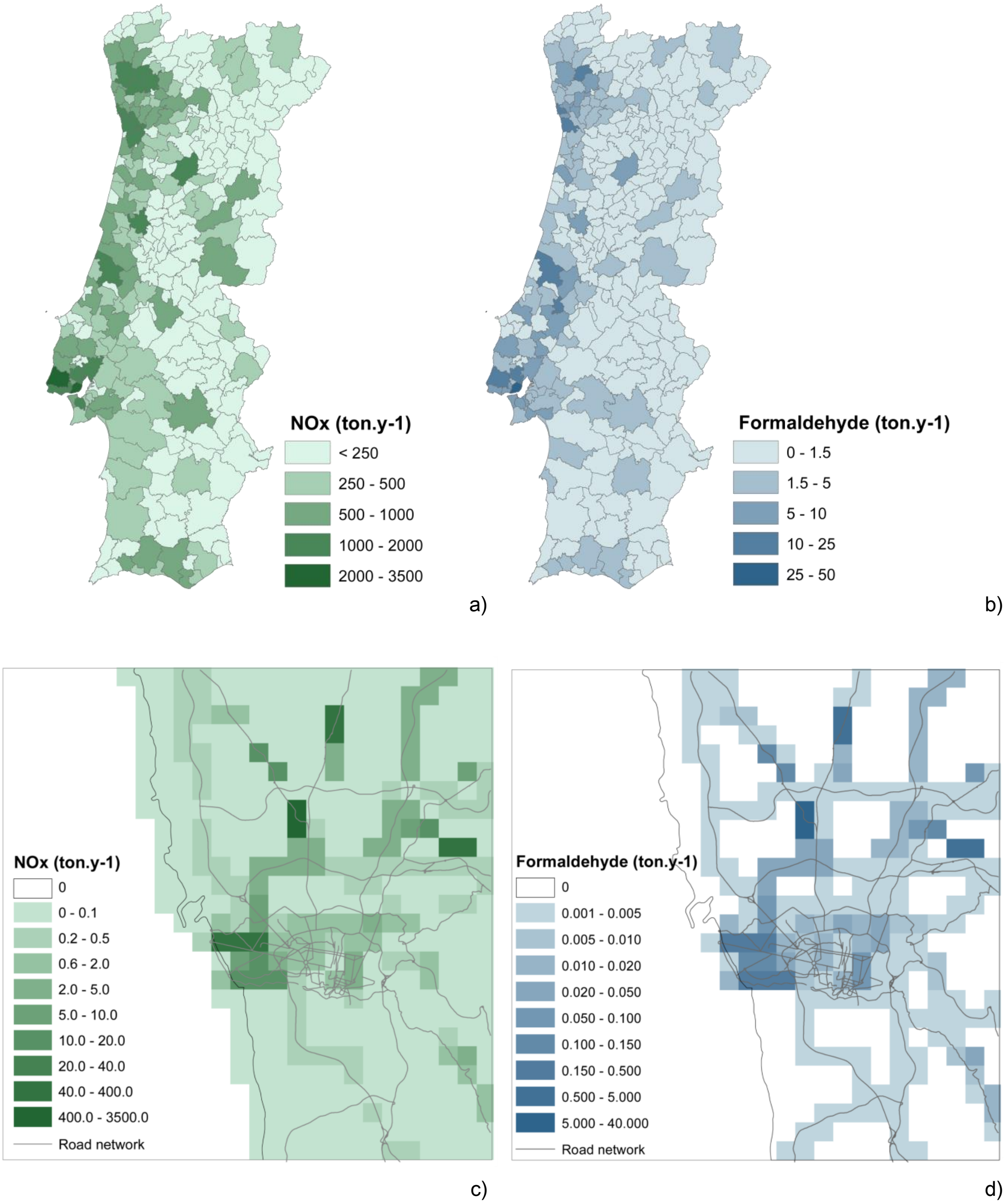


Figure 4.6 - Road-transport NOx (a,c) and formaldehyde (b,d) emissions for Portugal and for the Porto urban area (in a grid of 1×1km²), regarding the REF scenario.

4.3 The B20 scenario

The B20 scenario considers that the fuel used in diesel vehicles is a blend with 20% (v/v) of biodiesel. This emission scenario was calculated based on REF values and on the emission variation factors summarized in Table 4.4 and Table 4.5, and discussed in detail within the sections 3.1 and 3.2. Wherever possible it has been taken into account the type of road to use the appropriated emission factor: emission factors related to complete driving cycles (NEDC and CADC, Figure 3.3) were used for Portugal, while urban (UDC and CAU) and extra-urban (EUDC, CAR and CAM) factors from specific slices of the driving cycles were considered on the Porto urban area case study.

Table 4.4 - Average emission variations (%) of regulated pollutants for an EURO 4 LPV over the NEDC and CADC (Bakeas et al., 2011) and for an EURO 5 LPV over the NEDC (Lopes et al., 2014).

Pollutant	EURO 4	EURO 5		
	Avg (NEDC;CADC)	UDC	EUDC	NEDC
NOx	5.92	-20.36	-4.09	-10.83
NO	-	*-69.92*	*-13.82*	*-29.44*
NO_2	-	*1.28*	*8.12*	*4.52*
PM10 / PM2.5	-3.42	-	-	-61.57
HC	-8.13	1.21	4.13	2.38
CO	-16.98	-	-	-
CO_2	1.11	-0.23	3.55	1.46

Table 4.5 – Average carbonyl compound emission variations (%) for an EURO 4 LPV over the NEDC and CADC (Karavalakis et al., 2011b) and average benzene* emissions at different engine loads for an EURO 4 LPV (Di et al., 2009).

Pollutant	NEDC	CAU (0.20 MPa)	CAR (0.38 MPa)	CAM (0.55 MPa)
Formaldehyde	18.03	25.80	19.96	23.97
Acetaldehyde	23.57	22.67	16.58	22.80
Acrolein/acetone	45.97	28.02	34.52	46.07
Benzene*	-	37.75	4.21	1.42

The total pollutant emissions estimated for the B20 scenario and for both case studies are presented in Table 4.6.

Table 4.6 – Annual pollutant emissions (ton) estimated for road-transports in Portugal and Porto urban area, regarding the B20 scenario.

Pollutant	Emission (ton)	
	Portugal	Porto urban area
Acrolein	177	68
Benzene	257	91
Acetaldehyde	352	129
Formaldehyde	664	247
PM2.5	4523	2445
PM10	5009	931
NMVOC	20464	3608
CO	20807	11145
NOx	102586	29184
CO_2	17589714	7272492

Since the spatial distribution of B20 emissions is similar to the REF ones the spatial distribution of B20 emissions is not presented here. However, the comparison between both emission scenarios is shown in section 4.4.

4.4 Emission scenarios comparison

The variations of the total emissions estimated for REF and B20 scenarios are presented in Figure 4.7. The emission variations found between both study areas are mainly due to different methodologies and input data used for each of them, including the emission factor, which are function of the driving cycles that characterize each study area (complete driving cycles for Portugal and specific emission factors taking into account the road network information for the Porto urban area).

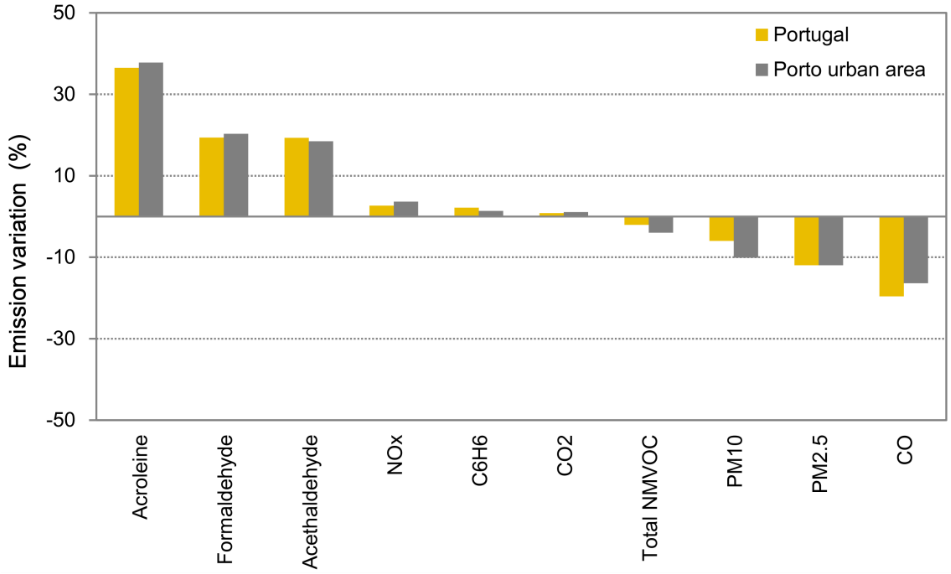


Figure 4.7 – Emission variations (%) between B20 and REF scenarios [(B20-REF)/REF].

According to the Figure 4.7, three pollutant groups can be identified. The first group is composed by carbonyl compounds (acrolein, formaldehyde and acetaldehyde), for which an increase of more than 20% in emissions was estimated when using B20 fuel. The second group comprehends NOx, C_6H_6, CO_2 and NMVOC which emissions vary in a small range [-3.98 ; 3.65]% for both domains. The third group includes CO, PM2.5 and PM10 which emissions are reduced when B20 is used instead of pure diesel, varying between [-19.60 ; -5.96]%. The higher reduction regards to CO, being the B20 emissions almost 20% lower than REF emissions for Portugal and 16% lower for the Porto urban area). PM10 and PM2.5 emission differentials for B20 are about 10% lower than for REF over both domains. The results obtained for regulated pollutants are in accordance to previous works over the Northern region of Portugal (Ribeiro et al., 2011, 2012).

The representativeness of the estimated variations in total emissions (APA, 2011) for each pollutant and case studies are compiled in Table 4.7.

Table 4.7 - Representativeness of the estimated variations (B20-REF) in total emissions regarding the studied pollutant, for Portugal and the Porto urban area (APA, 2011).

Pollutant	Portugal (%)	Porto urban area (%)
NOx	0.94	1.89
CO_2	0.26	0.41
Total NMVOC	-0.07	-0.54
PM10	-0.30	-0.81
PM2.5	-0.66	-1.04
CO	-4.98	-5.31

According to Table 4.7, the use of B20 on road transports represent a variation in total emission inferior that 1% for both case studies, with exception for CO (~5%) and NOx and PM2.5 over the Porto urban area (~2%).

As already discussed in section 3.1.5, the use of biodiesel/diesel blends in road transports increase aromatic hydrocarbon and aldehyde emissions that are especially important due to their reactivity, potentiating tropospheric ozone formation and rising of the probability of cancer, among other health disease. Figure 4.8 and Figure 4.9 show the spatial distribution of these pollutant emissions (a-d) over Portugal and the Porto urban area respectively, as well as the equivalent ozone production (EOP, see section 3.1.5) (e) regarding the difference between B20 and REF scenarios (B20-REF). The population which is potentially exposed to these pollutants is presented in Figure 4.8f) for Portugal and in Figure 4.9f) for the Porto urban area.

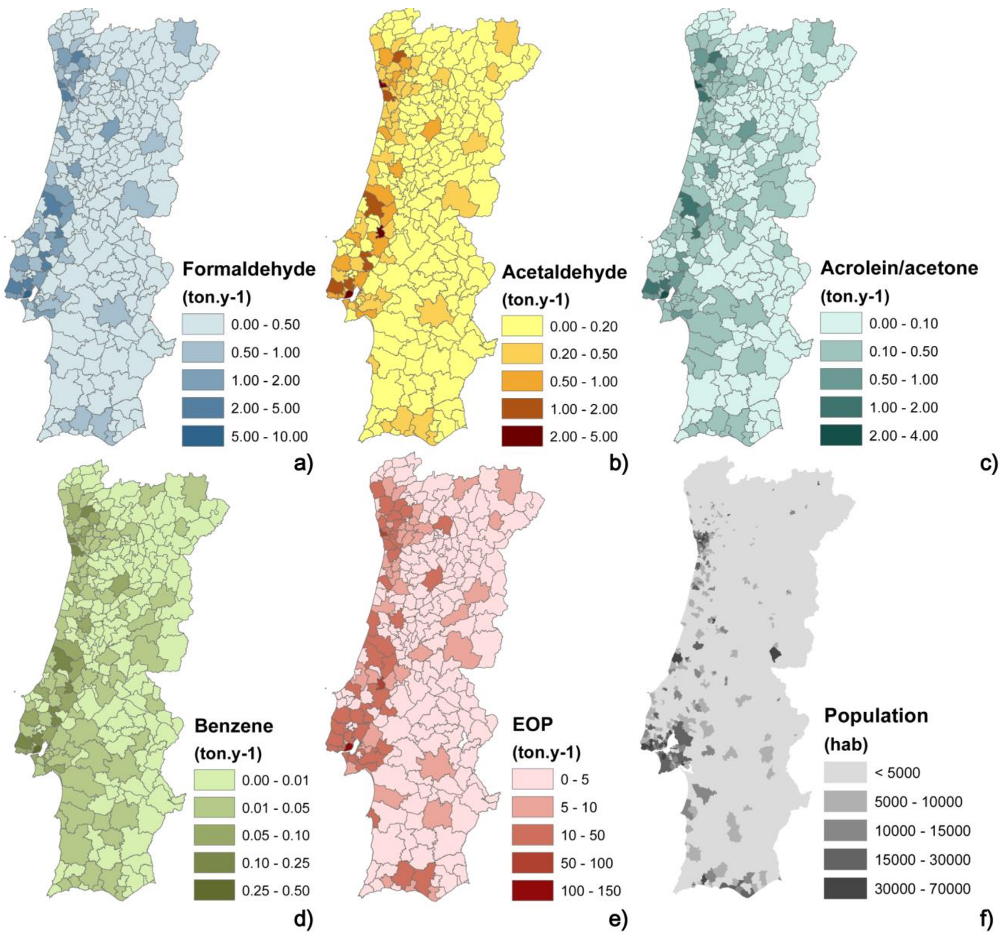


Figure 4.8 – Difference between REF and B20 annual emissions (ton·y^{-1}) of: a) formaldehyde, b) acetaldehyde, c) acrolein/acetone and d) benzene; e) increment on Equivalent Ozone Production (EOP) by the use of B20 and f) population distribution, over Portugal.

As expected, the replacement of pure diesel by B20 increases the non-regulated pollutant emissions especially over the urban areas and coastline of Portugal were the population is greater (Figure 4.8) and the fuel consumption is higher (Figure 4.4). The EOP from benzene and carbonyl compounds is especially important in urban areas, increasing the ground level ozone and potentiating the occurrence of photochemical smog.

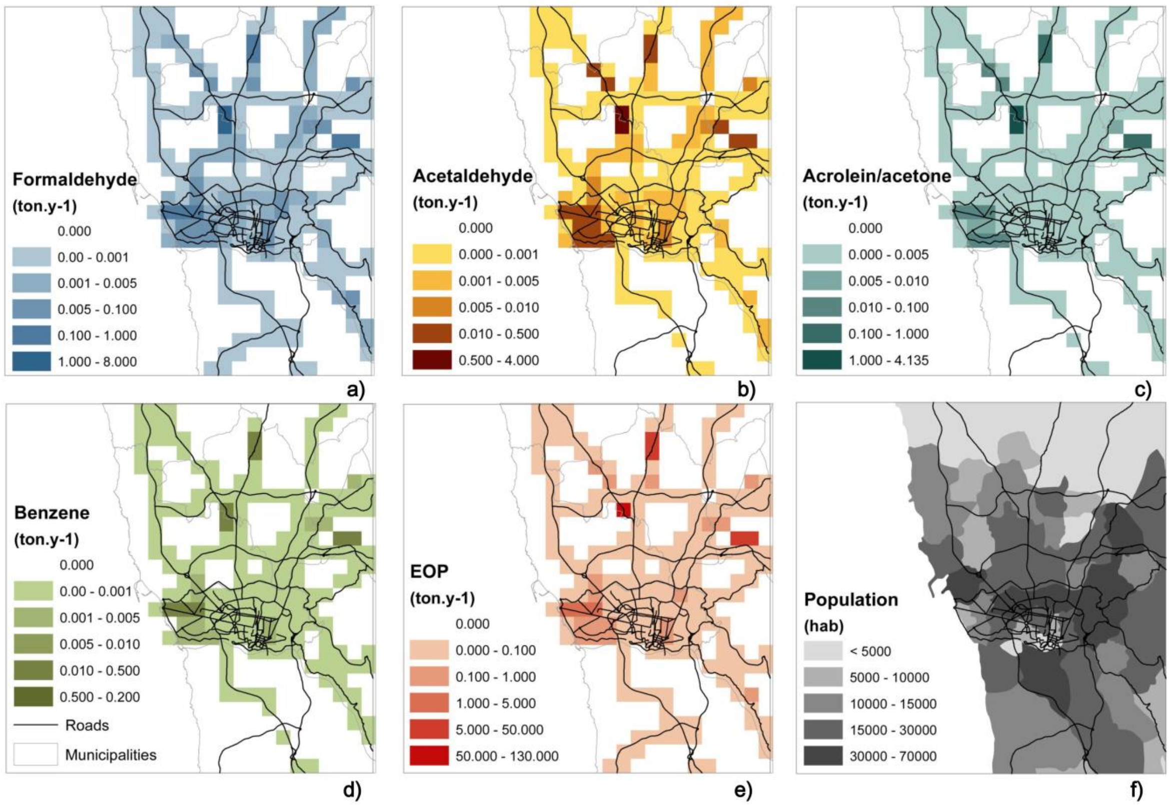


Figure 4.9 – Difference between REF and B20 annual emissions (ton·y^{-1}) of: a) formaldehyde, b) acetaldehyde, c) acrolein/acetone and d) benzene; e) increment on Equivalent Ozone Production (EOP) by the use of B20 and f) population distribution, over the urban area of Porto.

Regarding the urban area of Porto (Figure 4.9), results point out that if B20 fuel is used instead of conventional diesel, the pollutant emissions increase significantly (Figure 4.7). Due to their maximum incremental reactivity value (MIR, see Figure 3.5) and emission amounts, formaldehyde is the most critic pollutants among the non-regulated pollutant studied, which emissions increment from the use of B20 contributes to 58% of the EOP over the entire domain, while the contribution of benzene is insignificant (0.25%) and the remaining pollutants effect the total EOP in about 20%. Figure 4.9 also reveals that the hot spots are located at West and at North of the city, where the road traffic is higher.

4.5 Synthesis

In order to assess the impact of a 20% of biodiesel blended with petroleum-based diesel over Portugal and the Porto urban area, two emission scenarios were built (REF and B20). The TRansport Emission Model for line sources (TREM) was applied to estimate the emissions for both mentioned scenarios. The input data required by TREM includes information about the traffic fluxes, the vehicle fleet distribution and the road network.

The difference between REF and B20 scenarios includes the fuel characteristics used by diesel engines: REF scenario considers that the conventional diesel is used by the road-transport sector, while B20 assumes that the diesel is blended with 20% (v/v) of biodiesel. Thereby, the B20 scenario was built based on REF and the application of updated emission factors according to the approached presented in sections 3.1 and 3.2.

The results obtained suggest that the introduction of 20% of biodiesel in petroleum-based diesel in road transportation promotes a reduction in PM10, PM2.5 and CO emissions over Portugal and urban area of Porto. However, the changes on emissions represent less than 1% regarding the total emissions, with exception for CO, with emission variations can reach to 5% in both case studies.

On the other hand, an increase on NOx and non-regulated pollutants emissions, such as acrolein, formaldehyde and acetaldehyde, was observed, potentiating tropospheric ozone formation and eventually causing adverse effects on human health.

In order to predict the effects of biodiesel use and its emissions on air quality over both study domains, air quality modelling studies were performed, especially to investigate the impacts on PM10, PM2.5 and O_3 atmospheric concentration levels, which are currently the most current critical pollutants in terms of exceedences of legislated values. This work will be addressed in Chapter 7.

Chapter 5. The air quality modelling system

This fifth chapter focused on the selection and description of the numerical and mesoscale air quality modelling system that will be used to investigate the impacts of biodiesel use for road transports on air quality over Portugal and the Porto urban area. The selection of the WRF-EURAD air quality modelling system was based on a multi-model comparison exercise that is addressed in section 5.1. A detailed description of the selected modelling system is addressed in section 5.2.

5.1 Selection of the modelling system

The selection of the air quality modelling system to be applied in this study was supported by the national project "ENSEMBLAIR – Improving air quality assessment with ensemble modelling" (Monteiro et al., 2013a, 2013b). This project aimed to reduce the uncertainty on numerical chemical transport models results through the applications of ensemble techniques. To achieve this objective five chemical transport models were selected and their results were compared within a multi-model comparison exercise (Monteiro et al., 2013a). The models were select based on a state of the art revision of regional chemical transport models. The selection criteria were focused on models applicability and tests over Portugal; the availability of spatially resolved modules for anthropogenic and biogenic emissions as well as a complete chemical mechanism. The selected models include CHIMERE (Schmidt et al., 2001; Bessagnet et al., 2004), EURAD (Elbern et al., 2007), LOTOS-EUROS (Schaap et al., 2008), CAMx (Tesche et al., 2006) and TAPM (Hurley et al., 2003). All of them are mesoscale models designed for short and long-term simulations of oxidants and aerosol formation, through different degrees of complexity, as discussed by Monteiro et al. (2013a).

The five models were applied in their optimized set up regarding input data, parameterization and boundary conditions, and considering an horizontal resolution of 5 × 5 km^2. The Portuguese anthropogenic emissions inventory (INERPA, APA, 2011) was used as a common basis for all models, and models were meteorologically driven by the "Weather Research and Forecasting Model" (WRF, Skamarock et al., 2008), excepting TAPM that has an own meteorological data base coupled. All models were applied to over July 2006, with a spin-up time period of 1-2 days.

The multi-model evaluation and comparison exercise was focused on O_3 and PM10 concentrations, due to the common exceedences of limit values of these two pollutants over mainland Portugal. This exercise was supported by observed data from 22 background stations (including urban, suburban and rural environments) from the national air quality monitoring network[3]. Three statistical parameters, described in detail in section 6.2 and Table 6.2, were chosen to evaluate the five models performance: the correlation factor (R) indicates the correspondence of timing and evolution between observed and simulated concentration values; the root mean square error (RMSE) gives information about the skill in predicting the magnitude of a pollutant concentration; and the systematic error (bias) which translate the average difference between simulated and observed values (negative for overestimations and positive for underestimations).

According to the multi-model performance assessment (Monteiro et al., 2013a) the model with more robust prediction skills was the EURAD model (Elbern et al., 2007), having presented higher correlation factors and lower RMSE values for O_3 (R = 0.64, RMSE = 28.92 $\mu g \cdot m^{-3}$) and PM10 (R = 0.51, RMSE = 19.76 $\mu g \cdot m^{-3}$) surface concentrations. Based on this result, EURAD was selected to perform the air quality simulations to assess the impact of biofuels on air quality over Portugal and Porto urban area.

Additionally, all of the applied models were found to have significant biases for both pollutants, indicating an overestimation of ozone (bias values range from -45.0 $\mu g \cdot m^{-3}$ to 6.7 $\mu g \cdot m^{-3}$ for TAPM and EURAD, respectively). A different picture was obtained for PM10, with positive bias values for all selected models ranging from 7.0 $\mu g \cdot m^{-3}$, for TAPM, to 22.0 $\mu g \cdot m^{-3}$ for LOTOS-EUROS, pointing out to an underestimation of PM10 concentrations.

[3] For more information about the selected monitoring sites, see Monteiro et al. (2013a), and section 5.3.2 for detailed information regarding the national air quality monitoring network.

5.2 WRF-EURAD modelling system

The WRF-EURAD is an Eulerian modelling system with the structure presented in Figure 5.1, consists on the following three major models:

- **The Weather Research & Forecasting (WRF)** model (Skamarock et al., 2008), version 3.5.0, acts as meteorological driver for the CTM, delivering the meteorological fields needed (e.g. wind, relative humidity and temperature);
- **The EURAD Emission Model (EEM)** (Memmesheimer et al., 1991) delivers emission fields for the specific grid used considering seasonal, weekly and diurnal cycles, as well as international holidays;
- **The EURopean Air pollution Dispersion – Chemistry Transport Model (EURAD-CTM)** (Hass, 1991; Ebel et al., 1997; Elbern et al., 2007) – version 5.6 – computes transport, chemical reactions and deposition of gas-phase and aerosol-phase species.

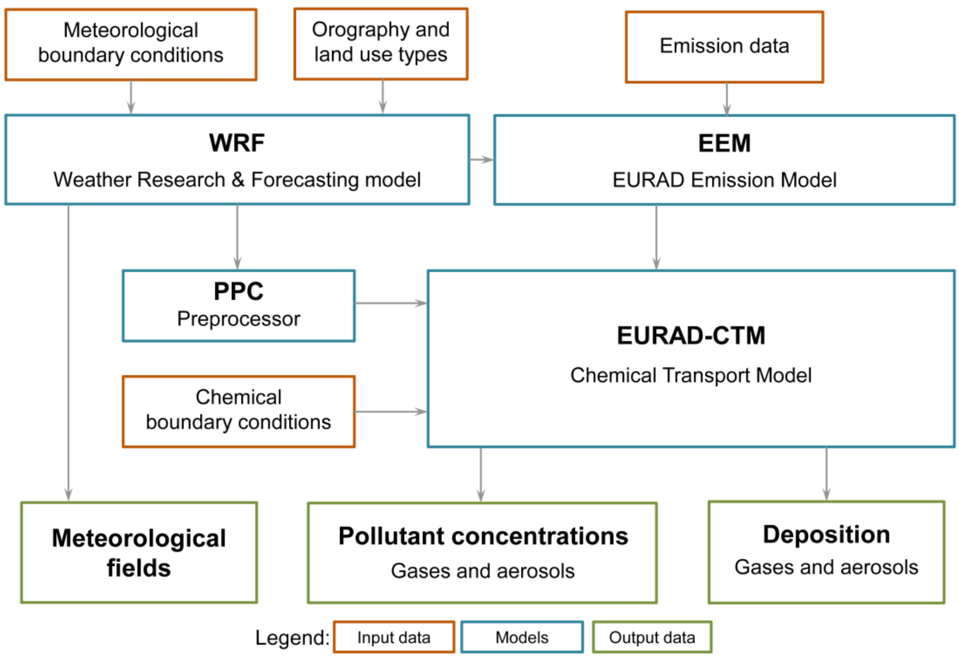


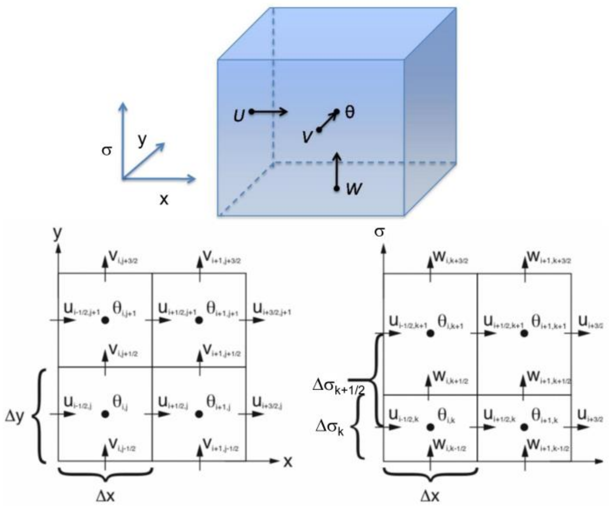
Figure 5.1 – Scheme of the WRF-EURAD air quality modelling system.

The input information needed to simulate air quality includes the orography and land use types for its specific geographical domain as well as the climatological boundary conditions to provide the meteorological condition fields produced by WRF model and to calculate biogenic emissions by EEM. Additionally, meteorological fields are processed by the pre-processor (PPC) in order to calculate additional meteorological information needed to the EURAD-CTM, that, together with biogenic and anthropogenic emissions, constitute the main input data for EURAD-CTM. The EURAD-CTM outputs include 3-D gases and aerosols deposition and concentrations fields.

In this section, the WRF-EURAD modelling system is described in detail in terms of the models that this system includes and its geometry as well as the modelling system setup and details of its application with in this study.

5.2.1 Geometry of the modelling system

Both WRF and EURAD-CTM use a Lambert conformal conic projection grid with an equidistant rectangular horizontal spacing. The state variables are represent according to the Arakawa C-Grid staggering (Arakawa and Lamb, 1977) (Figure 5.2a), what means that the *u* components are located at the centre of the left and right grid faces, and the *v* and *w* components at the centre of the upper and lower grid faces. Mass points, such as potential temperature, pressure, density, moisture variables, pollutant concentrations, among other variables, are defined in the centre of the grid cell. Vertically, the atmosphere is divided by terrain-following sigma coordinate layers defined by Equation 5.1. (Figure 5.2b)


a)

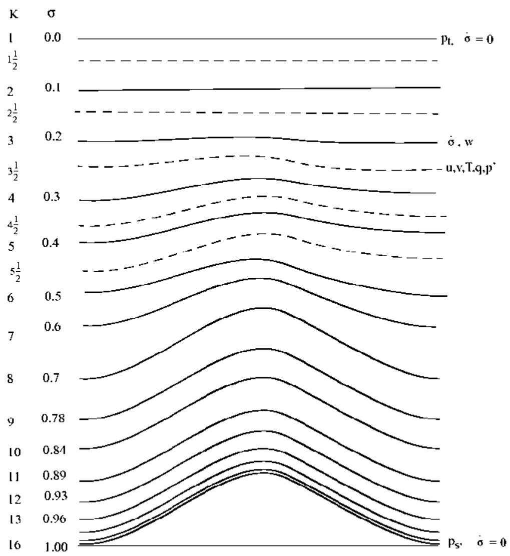

b)

Figure 5.2 – WRF-EURAD modelling system geometry: a) horizontal and vertical views of the Arawaka C-grid configuration; b) example of the vertical structure of a grid for 15 vertical layers (solid lines denote sigma levels and dashed lines denote half-sigma levels) (Skamarock et al., 2008).

$$\sigma_k = \frac{p_k - p_{top}}{p_{bot} - p_{top}}$$ **Equation 5.1**

Where:
k: layer number;
$p_{bot,k,top}$: Pressure at the surface, layer k and top of the model, respectively.

The geometry of the simulation domains used in this study is described in next section (5.2.1.1) regarding their vertical and horizontal structures and dimensions.

5.2.1.1 Geometry of the simulation domains

Based on previous applications of this modelling system (Nieradzik, 2011; Elbern and Friese, 2013), it was assumed that the atmosphere is divided into 23 terrain-following sigma coordinate layers. The top boundary of the WRF-EURAD is set at 100 hPa and the diffuse vertical fluxes at the top are set to zero. About 15 layers are defined above 2 km height and the Earth's surface defines the bottom boundary. The vertical structure of the atmosphere used within this modelling application is presented in Table 5.1.

Table 5.1 – The vertical structure of the WRF-EURAD grid, defined by terrain-following sigma coordinates.

Layer index	σ values	Pressure (hPa)	Height (m)
Surface	1.000	1013.25	0
1	0.995	1008.68	38
2	0.990	1004.12	76
3	0.985	999.55	115
4	0.980	994.99	153
5	0.970	985.85	231
6	0.960	976.72	309
7	0.945	963.02	427
8	0.930	949.32	546
9	0.910	931.06	708
10	0.890	912.79	872
11	0.865	889.96	1081
12	0.840	867.13	1294
13	0.810	839.73	1556
14	0.780	812.34	1825
15	0.740	775.81	2196
16	0.700	739.28	2581
17	0.600	647.95	3615
18	0.500	556.63	4775
19	0.400	465.3	6101
20	0.300	373.98	7658
21	0.200	282.65	9560
22	0.100	191.33	12064
23	0.000	100.00	16179

Since the pollutant concentrations variables are defined in the centre of the cells and the thickness of the lowest layer is about 38 m, the concentration pollutants extracted to the first level correspond to a height of approximately 19 m.

On air quality simulations is desired, in general, a high resolved look at physics and chemical states of the atmosphere in a certain region. To simulate only the region of interest would be a great loss of information since many tropospheric constituents are long-living and can be transported over large distances and information inflow from outside the area could not be considered this way. On the other hand, to simulate an area large enough to comprise all necessary sources with desired high resolution is not feasible due to computational limitations. To overcome these impasses, different domains with increasingly finer resolution are considered using nesting capacities.

In this study, the WRF-EURAD simulations were started on a grid with large extent, in a continental scale, covering Southern Europe and Sahara Desert, but with a low horizontal resolution of 125×125 km^2 (C125, the coarse domain). Inside C125, is defined a region around the area of the next domain to provide boundary conditions that need to be interpolated to the next smaller domain grid. The second simulation domain covers Iberian Peninsula with 25×25 km^2 of horizontal resolution (IP25). The same nesting process is applied to the third domain over Mainland Portugal, with 5×5 km^2 (PT05) and then to the last domain covering the Porto urban area with a fine horizontal resolution of 1×1 km^2 (OP01). The OP01 horizontal resolution is on the limit recommended by EURAD-CTM (Ebel et al., 1997; Monteiro et al., 2012).

Table 5.2 compiles all the information regarding domain dimensions and Figure 5.3 shows the simulation domains chain.

Table 5.2 – Dimensions of the simulation domains used in WRF-EURAD modelling system.

ID	Domain	Parent ID	Horizontal resolution (km)		Number of cells (WRF)		Number of cells (EURAD)	
			x	y	x	y	x	y
1*	C125	-	125	125	49	39	49	39
2	IP25	1	25	25	55	50	51	46
3	PT05	2	5	5	85	140	81	136
4	OP01	3	1	1	30	30	26	26

* Coarse domain

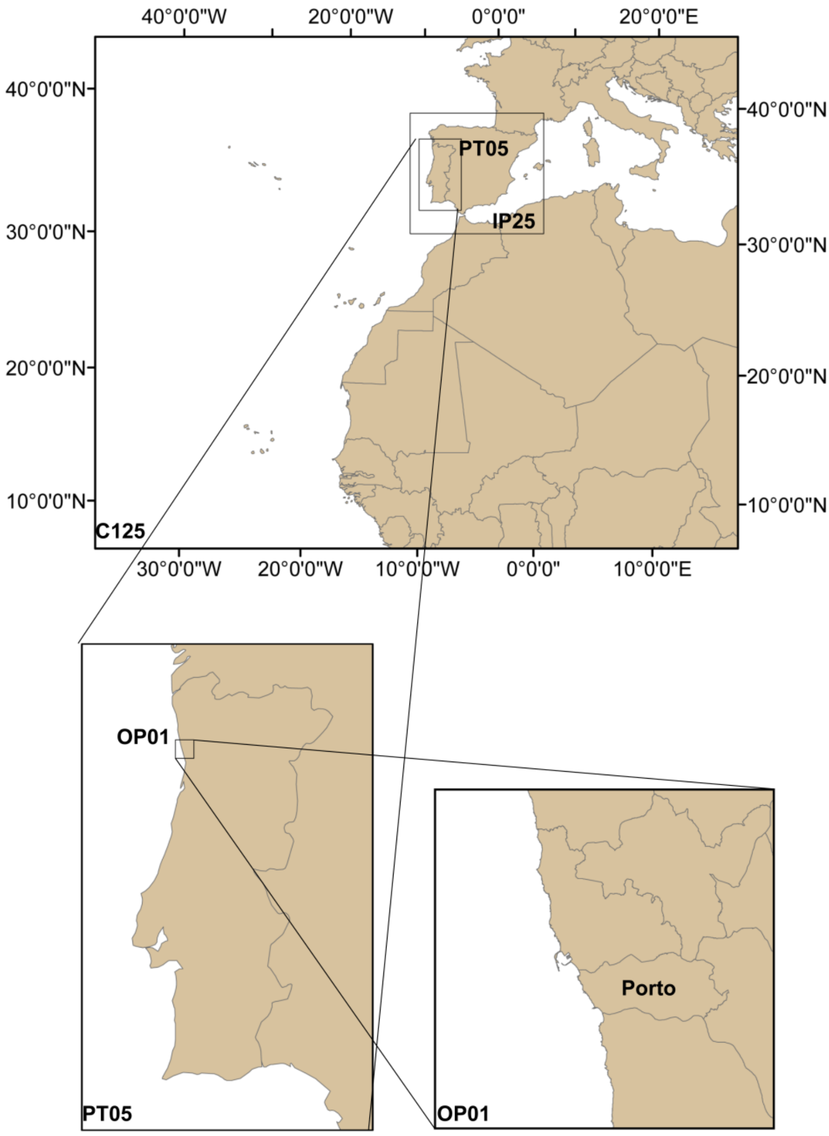


Figure 5.3 – Simulation domains used in the WRF-EURAD modelling system application.

With exception to the coarse domain, that has the same dimensions for WRF and EURAD simulations, the remaining simulation domains are not exactly the same for both models, but very similar (Table 5.2). In fact, WRF domains have two more cells in each side of the domain in order to better integrate the meteorological input on the CTM model.

5.2.2 Weather Research Forecasting model (WRF)

The WRF model (Skamarock et al., 2008) is a numerical weather prediction and atmospheric simulation system designed for both research and operational applications. Its dynamics solver integrates compressible and non-hydrostatic Euler equations.

A multi-agency[4] effort is on the basis of the WRF development to build a next-generation model and data assimilation system. Currently, WRF is a state-of-the-art model reflecting flexibility portable code, being efficient in computing environments ranging from massively-parallel supercomputers to laptop. It is suitable for a board span of applications from large-eddy (grid cell size >1 km) to global simulations (grid cell size >100 km). Such applications include real-time numerical weather predictions, data assimilation development and studies, parameterized-physics research, regional climate simulations, air quality modelling, atmosphere-ocean coupling and idealized simulations. WRF have been supported as a common tool for the universities/research and operational communities, and to facilitate the wide internationally use (Skamarock et al., 2008).

Here, a simplified description of the WRF model is given in the flow chart presented in Figure 5.4. Skamarock et al. (2008) and Wang et al. (2014) provide more detailed information regarding this model.

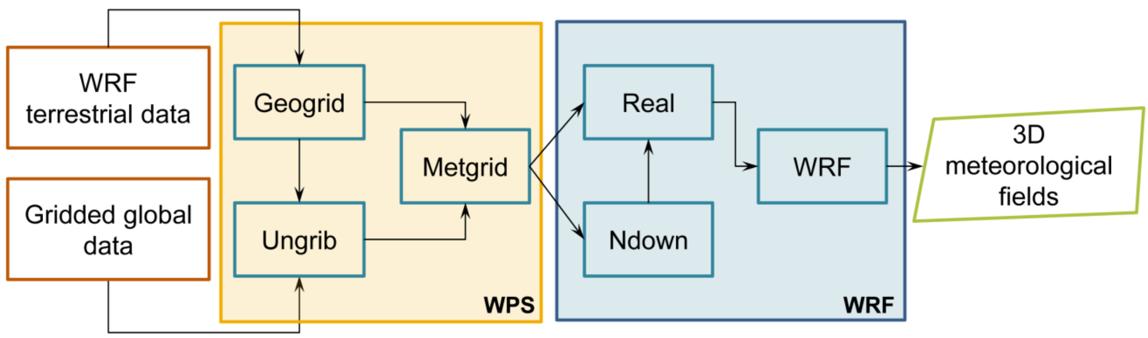


Figure 5.4 – WRF model flow chart (adapted from Wang et al., 2014).

To weather prediction, WRF needs topography and land-use for each domain, and meteorological global data to initialize the coarse domain simulation (Figure 5.4). Firstly, external data is prepared by the WRF Preprocessing System (WPS) throughout three programs (*Geogrid*, *Ungrib* and *Metgrid*) (Figure 5.4). The first program of the WPS chain is *Geogrid*, which defines model domain and interpolates static geographical data to the model domain grids. GRIB-formatted global data files contain several encoded variables

[4] The agencies that have been collaborating into the WRF development are: the National Center for Atmospheric Research's (NCAR) Mesoscale and Microscale Meteorology (MMM) Division, the National Oceanic and Atmospheric Administration's (NOAA) National Centers for Environmental Prediction (NCEP) and Earth System Research Laboratory (ESRL), the Department of Defense's Air Force Weather Agency (AFWA) and Naval Research Laboratory (NRL), the Center for Analysis and Prediction of Storms (CAPS) at the University of Oklahoma, the Federal Aviation Administration (FAA) and university scientists.

(more than are needed to initialize WRF). *Ungrib* uses "variable tables" (Vtables), provided with the software for common GRIB model output files, to identify the fields though codes. Then, *Ungrib* extracts needed meteorological fields from GRIB files and writes the data in a simple and WPS specific format (intermediate format). *Metgrid* horizontally interpolates the intermediate-format meteorological files extracted by *Ungrib* onto the simulation domains defined by *Geogrid*. The interpolated *Metgrid* output can then be ingested by the *Real* WRF program.

Like WPS, the WRF model also contains three programs, namely: *Real*, *Ndown* and *WRF* (Figure 5.4). *Real* reads the meteorological and static input information from the WPS and generate initial condition files. It vertically interpolates the required levels (Table 5.1) for the specified land surface scheme, in order to prepare soil fields for use into the model, and check if soil categories, land use, land mask, soil temperature and sea surface temperature are all consistent with each other. Additionally, *Real* generates initial condition files and processes multiple input time periods to generate the 3D lateral boundary conditions, namely u-, v- and w- wind components, potential temperature, vapour mixing ratio and geopotential height, which are couple with total column pressure. This program can run as either a serial or a distributed memory (parallel) job. For this work the second option was used. The *Ndown* program applies the nesting technique. WRF supports two nested options: 1-way nesting and 2-way nesting. 1-way nesting uses the output of a coarser grid simulation as input for the finer grid simulation, while 2-way nesting involves feedback from the fine domain to the coarse domain and vice versa (Misenis and Zhang, 2010). *Ndown* run in-between the coarser and finest domains in order to provide the initial and boundary conditions from the coarse together with input from higher resolution terrestrial fields provided by *Real* with regards to nest domain. In this work it was used the 1-way nesting technique because EURAD-CTM is not prepared to use other. Moreover, according to Misenis and Zhang (2010), that performed a comparison between these two nesting techniques, both reveal similar results and 2-way nesting requires more computational time. Finally, the *WRF* program provides 3D meteorological fields required by EURAD-CTM for each simulation domain, through numerical integration methods, based on data from previous programs.

The WRF setup used in this study is described in following section (5.2.2.1).

5.2.2.1 WRF model application

The global meteorological fields from the National (USA) Center for Environmental Prediction (NCEP/NOAA, 2000), which provides final (FNL) operational global data on 1º by 1º grids with a temporal resolution of six hours, were used to supply initial and boundary conditions for the coarse domain (C125). The FNLs are produced from the same model which NCEP uses in the Global Forecast System (GFS), however the FNLs are prepared about an hour after the GFS is initialized in order to observational data can be used. The FNL are available on the surface and at 63 sigma layers from 1000 millibars to 10 millibars. Parameters include surface pressure, sea level pressure, geopotential height, temperature, sea surface temperature, soil values, ice cover, relative humidity, u- and v- winds, vertical motion, vorticity and ozone (NCEP/NOAA, 2000). They are linearly interpolated to the WRF grid and linear time interpolation is also applied to obtain hourly values. For the other domains (not C125), the initial and boundary conditions come from the respective parent domain (Table 5.2 and Figure 5.3) and from the previous simulated day.

The WRF model has a large variety of physic parameterizations (described in detail in Wang et al. (2014)), namely regarding:

- Microphysics (mp_physics);
- Long- and shortwave radiation (ra_lw_physics and ra_sw_physics);
- Land and surface schemes (soil temperature and moisture) (sf_sfclay_physics and sf_surface_physics);
- Planetary boundary layer schemes (bl_pbl_physics);
- Cumulus parameterization (cu_physics).

Table 5.3 summarizes the selected physics options used in this study. Their selection was based on recommendations included in Wang et al. (2014), as well as on validation and sensitivity studies previously performed over Portugal (Aquilina et al., 2005; Carvalho et al., 2006) and over the Iberian Peninsula (Fernández et al., 2007).

Table 5.3 – Summary of WRF physic options used.

Physic parameter	Option	Domain ID
mp_physics	WSM 6-class graupel scheme (Hong and Lim, 2006)	1-4
ra_lw_physics	Rapid Radiative Transfer Model scheme	1-4
ra_sw_physics	Rapid Radiative Transfer Model scheme	1-4
sf_sfclay_physics	Pleim-Xiu surface layer (ARW only)	1-3
	Monin-Obukhov (Janjic) scheme	4
sf_surface_physics	Pleim-Xiu LSM (ARW)	1-4
bl_pbl_physics	ACM2 (Pleim) PBL (ARW) (Pleim, 2007)	1-3
	Mellor-Yamada-Janjic TKE scheme (Janjić, 1994)	4
cu_physics	Kain-Fritsch (new Eta) scheme (Kain, 2004)	1-3
	no cumulus	4

The WRF model generates several meteorological fields required by the EURAD-CTM, such as wind, temperature, water vapour mixing ratio, cloud liquid water content, 2 m temperature, surface heat, moisture fluxes and precipitation.

5.2.3 EURAD Emissions Model (EEM)

The EURAD Emission Model (EEM) aims to estimate proper emission data for the CTM simulations. The EEM converts annual anthropogenic emission (ton·year^{-1}) of CO, NH_3, NMVOC, SOx, NOx, PM2.5 and PMcoarse for each anthropogenic source-sectors, the so-called SNAP[5] codes, into g·s^{-1} grid box, following seasonal, weekly and diurnal variations. The time-profiles used are shown in Figure 5.5.

[5] SNAP1 – Combustion in energy and transformation industries; SNAP2 – Non-industrial combustion plants; SNAP3 – Combustion in manufacturing industry; SNAP4 – Production processes; SNAP5 – Extraction and distribution of fossil fuels and geothermal energy; SNAP6 – Solvent use and other product use; SNAP7 – Road transport; SNAP8 – Other mobile sources and machinery; SNAP9 – Waste treatment and disposal; SNAP10 – Agriculture.

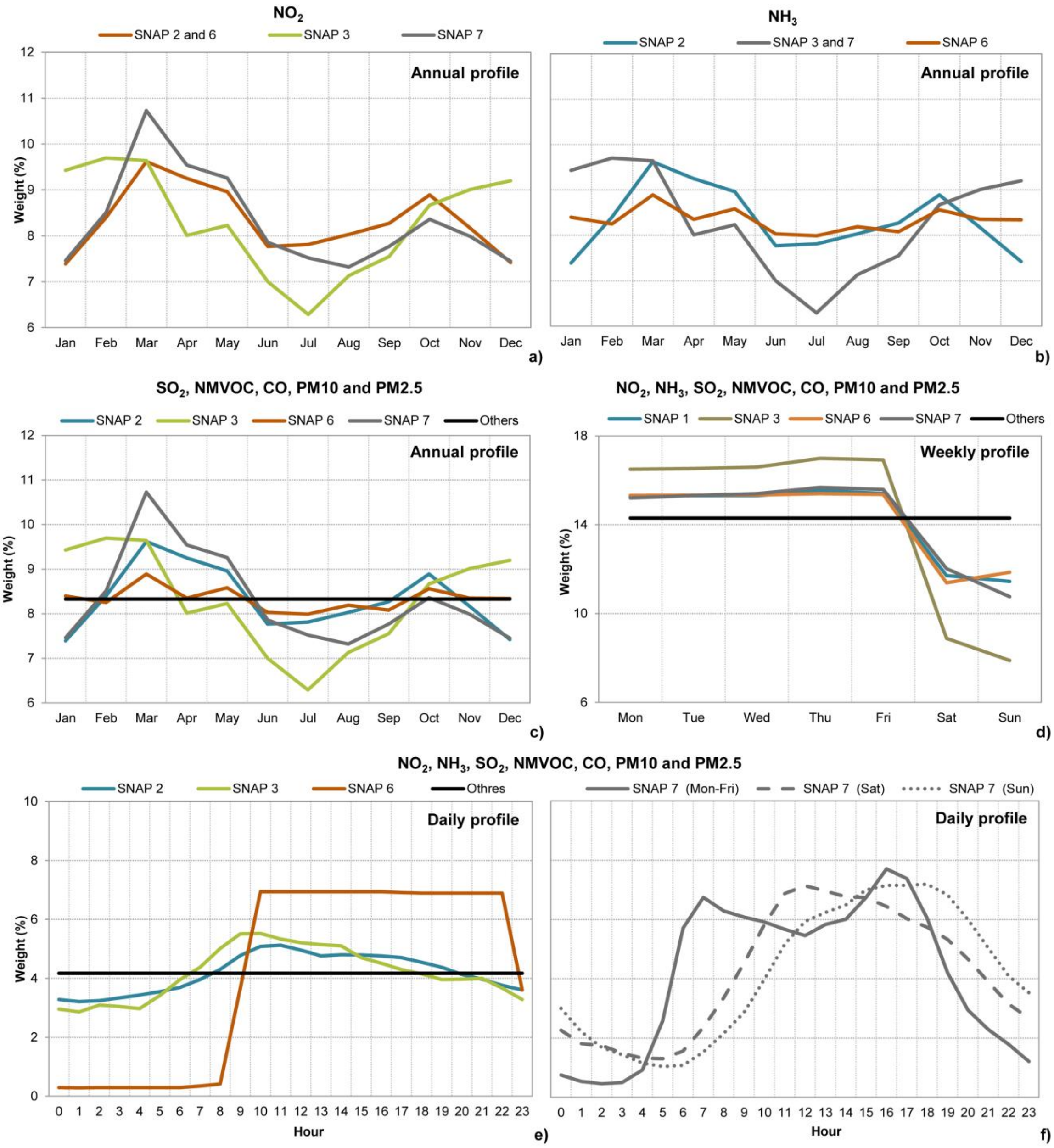


Figure 5.5 – EEM time-profiles defined by EMEP for SNAPs and pollutants: a-c) annual profiles; d) weekly profiles and e-f) daily profiles.

The time-profiles defined by EMEP and used in EEM, suggest a larger share of emissions during the winter months in the annual profiles (Figure 5.5a-c), especially for activity sectors involving combustion (SNAP 2, 3 and 7), as well as during working days in relation to the weekend (Figure 5.5d). Regarding the daily profiles (Figure 5.5e-f), a difference between day and night periods is well marked, especially for the transport sector (SNAP 7, Figure 5.5f), which daily profile identifies two rush hour (7-9h and 17-19h) on working days. During the weekend there is only a peak at lunch time on Saturday and another one on Sunday evening.

Besides time-profiles, emissions are also vertically allocated. The vertical profile (Table 5.4) adopted in EIRAD-IM modelling system is in accordance to a default distribution based upon plume-rise calculations performed for different types of emission source which are thought typical for different emission categories, under a range of stability conditions (EMEP, 2013).

Table 5.4 – Vertical distribution of anthropogenic emissions: percentage of each SNAP (S) sector allocated to the vertical layers of the EURAD-CTM (EMEP, 2013).

height (m)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
782-1106	17	0	6	0	0	0	0	0	0	0
523-781	29	0	30	0	0	0	0	0	0	0
325-522	46	0	41	0	0	0	0	0	35	0
185-324	8	0	19	0	0	0	0	0	40	0
93-184	0	50	4	10	10	0	0	0	15	0
0-92	0	50	0	90	90	100	100	100	10	100

Legend: 0%; 1-30%; 31-60%; 60-99%; 100%

The vertical profiles presented in Table 5.4 reveals that emissions from SNAP 4, 5, 6, 7, 8, and 10 are mostly in the surface layer (0-92 m), while energy production (SNAP 1) and combustion in manufacturing industry (SNAP 3) emit at higher altitudes (93-1106 m).

The emission specie groups of NMVOC, NOx, SOx and PM emissions that enter into the EEM as input files are split into single compounds, namely:

- NOx: NO and NO_2
- SOx: SO_2, H_2SO_4
- NMVOC: alcohols, esters and alkynes (low, medium and high HO rate constant), ethane, ethane, primary and internal alkenes (including allenes), formaldehyde, aldehydes, ketones, toluene, xylene, butadiene and other anthropogenic diens, acid and higher acids, limonene and gyoxal
- PM: Elemental carbon, organic carbon and PM for post number distribution.

Biogenic emissions do not enter into modelling system as input files. However, they are calculated in a module of the EEM, according to the given atmospheric condition (temperature, radiation, wind) and the given land use type, and following Guenther et al. (1993) approach.

The emission databased used within this study for Portugal and Porto urban area for the REF scenario is from the national emission inventory (APA, 2011), as discussed in section 4.2.

5.2.4 EURopean Air Pollution Dispersion – Chemical Transport Model (EURAD-CTM)

The EURAD-CTM (Hass, 1991; Ebel et al., 1997; Elbern et al., 2007) is a comprehensive Eulerian chemical transport mesoscale model in a non-hydrostatic configuration. The model's nesting facility enables to telescope from 1000 km to 1 km of horizontal resolution, allowing the combination of both high grid resolutions and the representation of large-scale transport processes. As already mentioned, anthropogenic and biogenic emissions temporally disaggregated from EEM, static geographical data of the simulation domains (geogrid file, from WPS), as well as meteorological fields from WRF and processed by the PPC, are the key information for the EURAD-CTM simulates transport, chemical transformation and deposition of tropospheric constituents (Figure 5.6).

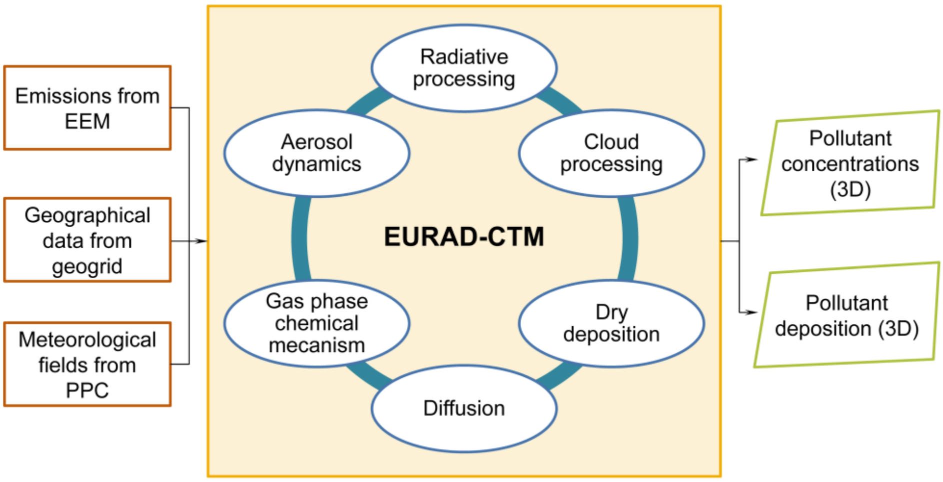


Figure 5.6 – Scheme of the EURAD-CTM model.

The chemistry is calculated on a fixed three-dimensional (3D) grid and transport is simulated as fluxes through the boundaries of each grid cell. As a CTM, the model simulates advection and diffusion, chemical conversion and deposition of trace gases and aerosols in the atmosphere (Nieradzik, 2011) thought solving mass conservation equation (Equation 5.2,(Hass, 1991).

$$\frac{\partial c_i}{\partial t} = -\nabla(uc_i) + \nabla(K\nabla c_i) + \frac{\partial c_i}{\partial t}|_{chem} + E_i + F_i + \frac{\partial c_i}{\partial t}|_{cloud} + \frac{\partial c_i}{\partial t}|_{aerosol} \qquad \text{Equation 5.2}$$

Where:

C_i: is the mean concentration of the specie *i*

$-\nabla(uc_i)$: Advection, that is transport by wind, where *u* is the vector of wind velocity

$\nabla(K\nabla c_i)$: Turbulent diffusion, with the tensor of turbulent diffusion *K*

$\frac{\partial c_i}{\partial t}|_{chem}$: Chemical conversion in the gas phase

E_i: Emission rates

F_i: Sum of the following fluxes:

- $F_{i,emis}$: Flux by emissions from the surface
- $F_{i,dep}$: Flux by dry deposition to the surface

$\frac{\partial c_i}{\partial t}|_{cloud}$: Aqueous chemistry, transport in clouds and wet deposition

$\frac{\partial c_i}{\partial t}|_{aerosol}$: Aerosol chemistry processed in Modal Aerosol Dynamics Model for Europe (MADE)

To initialize the simulation, latitude-dependent vertical profiles of the transported species are equally distributed over the whole coarse domain. However, for short-lived species initial values are set to zero. In this sense, and according to Schell (1996), a spin up run of four or five days should be computed providing realistic 3D fields of initial values for the desired period-time. Nevertheless, a simulation can also be set up on existing restart files from previous simulations, on interpolated fields from a mother domain or from initial values from data assimilation (Nieradzik, 2011). With initial values and boundary conditions defined, the chemical and physical calculations take place according to parameterization options that are described in following (section 5.2.4.1).

5.2.4.1 Chemical and physics options

The EURAD-CTM has several chemical and physical options available to simulate deposition, chemical transformations and transport of the pollutants on the atmosphere, namely regarding:

- Photolysis frequencies;
- Cloud processing;
- Dry deposition;
- Diffusion;
- Aerosol dynamics;
- Gas phase chemical mechanism;
- Data assimilation (not used in this study);
- Pollen module (not used in this study);
- EURAD-Fire-Model (not used in this study).

The chemical and physical options available to EURAD-CTM simulations are compiled in the model's run-script file, which an excerpt is shown in Figure 5.7. The options selection has also place in this run-script file.

```
# ================================= CTM configuration ===================================
#
# DATASS:    variational data assimilation
#            = 0: no
#            = 1: 1D-VAR (not yet available...)
#            = 2: 2D-VAR (not yet available...)
#            = 3: 3D-VAR
#            = 4: 4D-VAR
# PHOTO:     Method for calculation of photolysis frequencies
#            = 1: S. Madronich (offline)
#            = 2: A. Ruggaber  (online)
#            = 3: S. Madronich (online)
#            = 4: FTUV (online)
# CLOUD:     Cloud module
#            = 0: no clouds
#            = 1: R2.6 version
#            = 2: R2.6 version with MM5 clouds (B.Roeben)
# MADE:      Aerosol dynnamics
#            = 0: Disable modal aerosol dynamics
#            Bit 1 = 1: Include modal aerosol dynamics
#            Bit  2  =  1:  modal  aerosol  dynamics  with  secondary  organic  aerosol
#             (SORGAM, Schell et al. 2001)
#            Bit 3 = 1: permit APC and HDMR of APC
#            Bit 4 = 1: permit natural particle sources
# POLLEN:    Pollen module
#            = 0: disable pollen module
#            = 1: enable pollen module
# CHEMISTRY: Choose kinetic chemistry mechanism
#            = radm2:      RADM2
#            = adradm2:    Adjoint version of the RADM2 mechanism
#            = euro_radm:  EURO_RADM + RADM-C
#            = racm:       RACM
#            = racm_soa:   RACM with extensions for secondary organic aerosol
#            = racm_mim:   RACM_MIM mechanism
#                         (RACM with updated isoprene degradation)
#            = racm_mim2:  RACM_MIM2 mechanism
#            = chest:      CHEST
#                         (RACM_MIM with extensions for stratospheric chemistry)
#            = tracer:     TRACER
#            = racm_radon: RACM_MIM with radon decay chain
# SOLVER:    Chemistry solver
#            = 1: QSSA
#            = 2: ros2 (Rosenbrock integrator with 2 stages)
#            = 3: radau5 (implicit Runge-Kutta method of order 5)
# EFM:       EURAD-Fire-Modell
#            = 0: off
#            = 1: on, emission model according to J. Hoelzemann
#            = 2: on, GFAS wildfire emission data
# DRYDEP:    Dry deposition module
#            Bit 1 = 1: enable Wesely (1989)
#            Bit 2 = 1: enable Zhang et al. (2003)
#=======================================================================================
```

Figure 5.7 – EURAD-CTM configuration options piece from the model run-script.

The set of parameterization options used herein was recommended for applications over Europe and Portugal (Borrego et al., 2011; Nieradzik, 2011; Monteiro et al., 2013a). A description of each selected parameterization is given following.

5.2.4.1.1 Photolysis frequencies

Tropospheric ultraviolet (UV) radiation is the driving force for all tropospheric photochemical processes, having the potential to break down molecules into free radicals (photolysis) and thus initiate reaction chains by which primary pollutants (hydrocarbons and NOx) react to form secondary pollutants such as peroxyacyl nitrates and tropospheric ozone. The radiative transfer model used by EURAD-CTM is based on the Tropospheric Ultraviolet-Visible Model (Madronich, 1987), for calculating the spectral irradiance, the spectral actinic flux and photodissociation coefficients (J-values).

5.2.4.1.2 Cloud processing

According to (Elbern and Friese, 2013), the sub-grid cloud scheme in the EURAD-CTM was derived from the cloud model in the EPA Models-3 Community Multiscale Air Quality (CMAQ) modelling system (Roselle and Binkowski, 1999). Cloud effects on both gas phase species and aerosols are simulated by the cloud module. The effects of sub-grid clouds on grid-averaged concentrations are parameterized by modelling the mixing, scavenging, aqueous chemistry, and wet deposition of a representative cloud within the grid cell. For all sub-grid clouds, a 1-hour live time has been assumed. Depending upon weather the pollutant participates in the cloud water chemistry and on the liquid water content, pollutant scavenging is calculated by two methods:

1. For those pollutants that are absorbed into the cloud water and participate in the cloud chemistry, the amount of scavenging depends on Henry’s law constants, dissociation constants, and cloud water pH;
2. For pollutants, which do not participate in aqueous chemistry, the model uses the Henry’s law equilibrium to calculate ending concentration and deposition amount.

The accumulation mode and coarse mode aerosols are assumed to be completely absorbed by cloud water and rain water. Some rapidly established equilibria between the gas and aqueous phase (HNO_3 ,N_2O_5, NH_3, O_3, H_2O_2, SO_2, formic acid, methyl hydrogen peroxide and peracetic acid) are superimposed on five irreversible reaction involving the oxidation of SO_2 to SO_3^{2-} (Walcek and Taylor, 1986).

5.2.4.1.3 Dry deposition

The deposition scheme devised by Zhang et al. (2003) has been employed to calculate dry deposition velocities of twenty gas phase species[6] using a model which considers the aerodynamic resistance, the quasi-laminar layer resistance and, the ground or canopy resistances, depending on land use characteristics.

5.2.4.1.4 Diffusion

An upstream algorithm (Bott, 1989) was chosen to calculate the horizontal and vertical advection. The calculation of vertical Eddy diffusion is based on the specific turbulent structure in the individual regimes of the planetary boundary layer (PBL) according to the PBL height and the Monin-Obukhov length (Holtslag and Nieuwstadt, 1986). The vertical diffusion is semi–implicitly discretised following Crank–Nicholson scheme, with the Thomas algorithm used as solver.

5.2.4.1.5 Gas phase chemical mechanism

The chemical mechanism selected within this work was developed by Geiger et al. (2003). It is based on the Regional Atmospheric Chemical Mechanism (RACM) combined with the Mainz Isoprene Mechanism (MIM, Poeschl et al., 2000). The RACM-MIM reflects an advanced description of the air chemistry of biogenic ozone precursors like isoprene and others. It treats 84 chemical species (as real species and condensed species classes) and contains 23 photolysis reactions and 221 chemical reactions of higher order, solved by a stage-2 Rosenbrock algorithm (Verwer et al., 1999).

5.2.4.1.6 Aerosols dynamics

To simulate the aerosols dynamics, the EURAD-CTM incorporates the Modal Aerosol Dynamics model for Europe (MADE, Ackermann et al., 1998), developed specifically to EURAD-CTM, that describes the physical and chemical processes concerning particles species.

The dynamical processes concerning size distribution are transport, nucleation, condensation, coagulation and evaporation, which are calculated taking into account the interaction with clouds, wet and dry deposition, emissions into the air and the gas phase

[6] Sulphur dioxide; Formaldehyde; Sulphuric acid; Acetaldehyde; Nitrogen dioxide; Methyl-Vinyl-Ketone; Ozone; Methacrolein; Hydrogene peroxide; Methylglyoxal; Nitric acid; Cresol; Nitrous acid; Formic acid; Pernitric acid; Acetic acid; Ammonia; Organic peroxides; Peroxyacetylnitrate and Organic nitrates.

chemistry. The particles in MADE are separated into two groups: fine and coarse particles. The aerosol species treated as fine particle are secondary inorganic aerosols, primary and elemental carbon, other unspecified material of anthropogenic origin, as well as anthropogenic and biogenic secondary organic species. The coarse particles consist on unspecified material of anthropogenic origin, sea salt and mineral dust.

The formation of secondary organic aerosols (SOA) is treated by the Secondary ORGanic Aerosol Module (SORGAM, Schell et al., 2001). To provide concentrations of ammonia and nitrate in both gas and particle phase, sulphate in the particle phase and the amount of liquid water, SORGAM includes an aerosol thermodynamic model (Analytical Predictor of Condensation – APC), which solves particle chemistry in the NH_4^+ - NO_3^- - SO_4^{2-} - H_2O system. The APC is implemented as a fully equivalent operational model version, using the High Dimensional Model Representation technique (HDMR, Nieradzik, 2005). Overall MADE delivers size distribution, number concentration and volume of the aerosol, dry and wet deposition and aerosol and gas phase mass concentrations.

For a more detailed information about MADE and HDMR, see Nieradzik (2011).

To summarize, the physic and chemical parameterization options selected to this application, based on recommendations from Borrego et al. (2011b), Nieradzik (2011) and Monteiro et al. (2013a), are compiled in Table 5.5.

Table 5.5 – Physic and chemical options used in EURAD-CTM.

Physic and chemical parameters	Option used
Method for calculation of photolysis frequencies	Tropospheric Ultra-Visible Model (Madronich, 1987)
Cloud module	R2.6 version, based on Roselle and Binkowski (1999)
Dry deposition module	Scheme from Zhang et al. (2003)
Diffusion module	Bott (1989) algorithm
Aerosol dynamics module (MADE)	MADE including APC and HDMR (Nieradzik, 2005)
Kinetic chemistry mechanism	RACM-MIM mechanism (Poeschl et al., 2000; Geiger et al., 2003)
Chemistry solver	Rosenbrock integrator with 2 stages (Verwer et al., 1999)

Chapter 6. Evaluation of the air quality modelling system

Air quality modelling systems describe mathematically innumerable physical and chemical processes that characterize the atmosphere. In addition, they must be able to adequately quantify species concentrations in the atmosphere (Dennis et al., 2010). However, the atmosphere is characterized by random processes that cannot be precisely described by numerical approached. Turbulence, which controls atmospheric dispersion, is one of these processes, promoting spatial and temporal variability on the observed concentration fields. Additionally, uncertainties in the input data and model formulation itself are also important factors that increase the uncertainty in the model outputs. Uncertainties associated to model formulation may be due to erroneous or incomplete representation of the dynamic and chemistry of the atmosphere, incommensurability, numerical solution techniques, and choice of modelling domain and grid structure. On the other side, uncertainties in the input data may include variability on emission sources and imprecise geophysical representation of the simulation domains. Therefore, model results should be properly evaluated and their uncertainties correctly estimated (Hanna et al., 1993; Borrego et al., 2008) before using model results.

Since a model is only useful if it reflects the behaviour of the real world atmospheric processes being its simulations within a pre-defined level of accuracy that is acceptable for the intended purpose of use, the quality of a model should be determined by validation, verification, and evaluation (Schlünzen and Sokhi, 2008).

Validation is defined by Schlünzen and Sokhi (2008), as the testing of the extent to which a model describes the phenomena it was developed for. Typically, model validations carry out on model development laboratories (e.g. wind tunnels) to produce validation datasets, or using monitoring datasets, to check the performance of the model for a specific application. For each particular case, the required data completeness (suitable size, temporal and spatial coverage, minimum number of data gaps and consideration of any compilation procedures that may have caused data to be eliminated), quality and accuracy of the model have to be specified. These requirements vary according to the intended model application, as well as the model properties, such as model scale and parameterizations.

Also in according to Schlünzen and Sokhi (2008), verification is the act of confirming that the model exhibits a specified behaviour for a given case (e.g. an air pollution episode), while the main goal of evaluation exercises is to demonstrate that the model is "performing adequately" when compared with observations (Dennis et al., 2010).

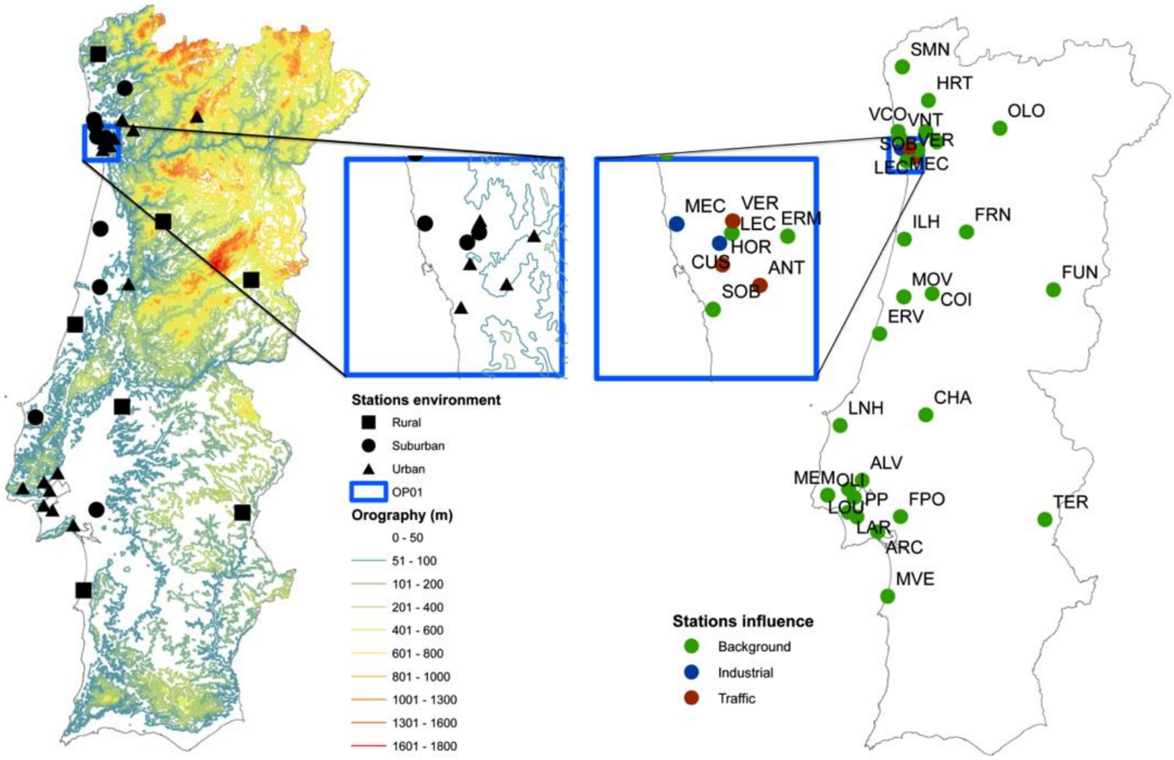
According to previous studies, including the multi-model comparison presented in section 5.1 (Djalalova et al., 2010; Borrego et al., 2011; Miranda et al., 2012; Monteiro et al., 2013a), air quality modelling systems results have important uncertainties associated, part of them related to systematic errors which could be removed or minimized through bias-correction approaches. A set of these techniques was tested and the main results are shown in section 6.2.

The WRF-EURAD modelling system evaluation (Dennis et al., 2010) is addressed in this chapter, generating statistics of the deviations between REF scenario unbiased modelling results and observations, comparing their magnitudes accordingly to a set of statistical parameters (section 6.2), for PT05 and OP01 simulation domains.

6.1 The air quality monitoring network

Observed data is essential information to validate an air quality modelling system. Thus, data from the air quality monitoring network of mainland Portugal (http://qualar.apambiente.pt/), with respect to the REF scenario year (2012), were used to evaluate the WRF-EURAD modelling system performance. The air quality monitoring network includes 68 stations classified as urban, suburban and rural regarding the type of environment and as background, traffic and industrial in terms of influence, following the classification in Garber et al. (2002). The air quality monitoring stations used for the model evaluation present a minimum data collection efficiency of 85% for each pollutant (CO, O_3, NO_2, PM10 and PM2.5), according to what is required by Air Quality Directive (2008/50/EC). A total of 28 stations with background influence (8 rural, 12 urban, and 8 suburban) were selected for the PT05 domain. The selection of only background influence stations is justified by the PT05 horizontal resolution (5×5 km^2) which is not sufficient detailed to correctly represent areas influenced by emissions from industrial or traffic activities (Monteiro et al., 2013a). On the other hand, 8 stations (5 urban, and 3 suburban) classified as industrial, background and traffic influence were selected for the OP01 domain, because the horizontal resolution of this domain is finer (1×1 km^2). Figure 6.1

shows the location and classification of the selected stations in the study domain. Note that the monitoring equipment follows a quality control/quality assurance procedure which guarantees validation and confidence in the use of these data.



a) b)

Figure 6.1 – Location and main characteristics of the selected monitoring stations for Portugal (PT05) and Porto urban area domains (OP01): stations environment and the terrain elevation (in m) (a); stations influence (b).

The pollutants measured in each monitoring station are listed in Table 6.1.

Table 6.1 – Monitoring stations selected and their classification (environment and influence and pollutants measured, for Portugal and Porto urban area domains (PT05 and OP01).

Abbreviation	Name	Type of environment	Type of influence	Pollutants					OP01
				CO	NO_2	O_3	PM10	PM25	
ALV	Alverca	Urban	Background	X	X	X	X		
ANT	Antas	Urban	Traffic	X	X		X		X
ARC	Arcos	Urban	Background	X	X	X	X		
CHA	Chamusca	Rural	Background		X	X	X	X	
COI	Coimbra - Inst. Geog.	Urban	Background			X	X		
CUS	Custóias	Suburban	Industrial		X	X	X		X
ERM	Ermesinde	Urban	Background		X		X		X
ERV	Ervedeira	Rural	Background		X		X	X	
FPO	Fernando Pó	Suburban	Background		X	X	X	X	
FRN	Fornelo do Monte	Rural	Background			X	X		
FUN	Fundão	Rural	Background		X	X	X	X	
HOR	S. Hora	Urban	Traffic	X	X		X		X
HRT	Horto	Suburban	Background		X	X	X		
ILH	Ílhavo	Suburban	Background		X	X	X		
LAR	Laranjeiro	Urban	Background	X	X	X	X	X	
LEC	Leça do Balio	Suburban	Background		X				X
LNH	Lourinhã	Suburban	Background			X			
LOU	Loures	Urban	Background		X	X			
MEC	Meco	Suburban	Industrial			X	X		X
MEM	Mem Martins	Urban	Background		X	X	X	X	
MOV	Montemor-o-Velho	Suburban	Background			X	X		
MVE	Monte Velho	Rural	Background	X					
OLI	Olivais	Urban	Background	X	X	X	X	X	
OLO	Lamas de Olo	Rural	Background		X	X	X	X	
PFR	Paços de Ferreira	Urban	Background		X	X	X	X	
PP	Paio Pires	Urban	Background			X			
SMN	S. Minho	Rural	Background		X	X	X		
SOB	Sobreiras	Urban	Background		X	X	X		X
STR	Sto. Tirso	Urban	Background		X	X	X		
TER	Terena	Rural	Background			X	X	X	
VCO	Vila do Conde	Suburban	Background		X	X	X		
VER	Vermoim	Urban	Traffic		X	X	X	X	X
VNT	Vila Nova da Telha	Suburban	Background		X		X		
			Total	**7**	**25**	**26**	**28**	**11**	**8**

6.2 Bias-correction approach

To increase the model skills and minimize model uncertainty, there are several techniques based on ensemble dispersion modelling (Galmarini et al., 2004; Wilczak et al., 2006; van Loon et al., 2007; Vautard et al., 2009; Monteiro et al., 2013b) and on methods for combining results from models and monitoring data (Borrego et al., 2011b; Denby and Spangl, 2010; McKeen et al., 2005; Monteiro et al., 2013). It is possible to combine these two types of data through methodologies that take into account physical laws (data assimilation) or that are based on a statistic or geometric way to combine data sources to create a new data set (data fusion) (Denby and Spangl, 2010). Examples of data fusion approaches are the bias-correction techniques which the objective is not to try to gain additional insight into model deficiencies or performance nor to correct artificially for them, but to remove potential systematic model errors intrinsic to each model formulation or input data. Bias-correction can be applied through different techniques, such as mean subtraction (McKeen et al., 2005; Wilczak et al., 2006), multiplicative ration adjustment (McKeen et al., 2005), hybrid forecast (Kang et al., 2005) and Kalman filter (Kang et al., 2005; Delle Monache et al., 2006; Djalalova et al., 2010), among others. Based on previous studies (Borrego et al., 2011; Monteiro et al., 2013a), three bias-correction techniques were applied to EURAD simulation results over Portugal: a Kalman filter (KF) technique, a subtractive/additive correction of the mean bias (SUBST, Equation 6.1) and a multiplicative ratio correction (RAT, Equation 6.2).

SUBST $$C^{corrected}(h, day) = -\frac{1}{ndays}\sum_{ndays}(C_h^{\mathrm{model}} - C_h^{obs}) + C^{\mathrm{model}}(h, day)$$ **Equation 6.1**

RAT $$C^{corrected}(h, day) = \frac{\sum_{ndays} C^{obs}(h, day)}{\sum_{ndays} C^{\mathrm{model}}(h, day)} \times C^{\mathrm{model}}(h, day)$$ **Equation 6.2**

The KF is a recursive, linear, and adaptive method that has been used recently to improve air quality forecasts of ground-based O_3 (Kang et al., 2005; Delle Monache et al., 2006, 2008; Djalalova et al., 2010; Sicardi et al., 2011). KF performance is sensitive to the error ratio between variances of white noise and random error, which indicates the way in which the KF responds to the variations in biases at prior steps. An optimal error ratio exists for generating the best prediction given the numerical modelling system and the dynamics of the study area. One way to estimate the optimal error is described by Kang et al. (2008) which consists in minimizing the RMSE and maximizing the correlation coefficient for all the stations and modelling system. SUBST (Equation 6.1) and RAT (Equation 6.2) corrections force the mean bias at each monitoring site to be zero, using the bias detected from the previous days for each particular hour (h) of the day. These three bias-correction procedures are model specific, site specific and time of day specific.

For the case of SUBST and RAT corrections, to estimate the previous days bias, different training periods were tested (Monteiro et al., 2013a): a 7 day training period was chosen as a compromise between having a sufficiently long period to gather adequate statistics, but not too long to mask seasonal variations in ozone, as discussed in Wilczak et al. (2006); and a 4 day period was also tested in order to distinguish different synoptic conditions, which are characterized by a 3-4 day period (Stull, 1988; Carvalho et al., 2010a; Tchepel and Borrego, 2010). This test revealed that the RAT technique with a 4-day training period is the most appropriate bias-correction approach to apply over Portugal, demonstrating significant improvements for both analysed pollutants (PM10 and O_3), as demonstrated by daily profiles for O_3 and PM10 in Figure 6.2.

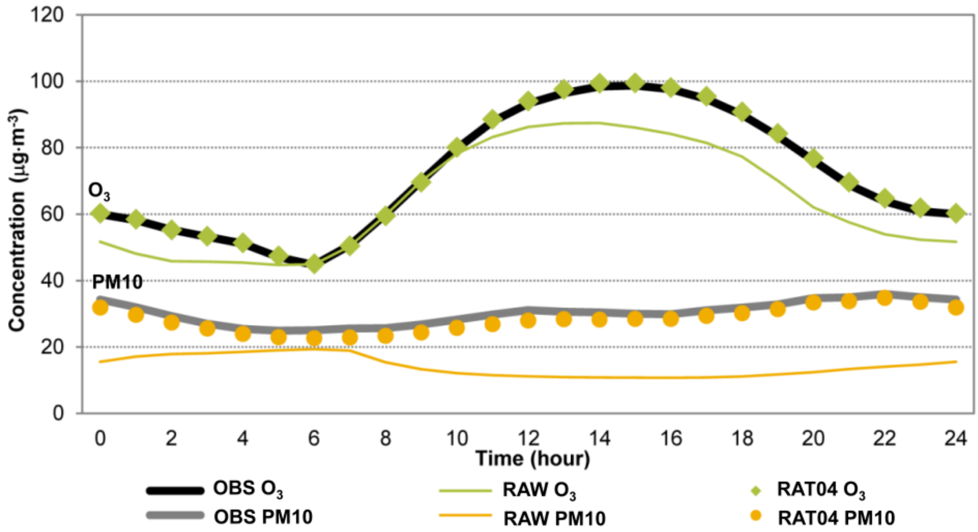


Figure 6.2 – Daily profiles, averaged over all monitoring stations, of observed values (OBS), EURAD simulations (RAW) and EURAD simulations with RAT04 correction (RAT04) for O_3 and PM10 (adapted from Monteiro et al., 2013a)

The improvement of the corrected data skill was measured by a bias reduction of 76 % for O_3, and 91 % for PM10, a decrease of RMSE in 14 % for O_3 and 32 % for PM10, and an improvement on the correlation factor of 14% for O_3 and 54% for PM10. In this sense, the RAT04 bias-correction technique will be applied to WRF-EURAD modelling system (described in detail in section 5.2) outputs in order to obtain more accurate simulation results to investigate the impact of biofuels for road traffic on air quality over mainland Portugal and the Porto urban area.

6.3 Operational evaluation of the WRF-EURAD modelling system

Within the framework for evaluating regional-scale numerical modelling systems developed by Dennis et al. (2010), operational evaluation refers to statistical and graphical analysis to determine whether modelling system estimates are in agreement with the observations in an overall sense, measuring the deviations and their magnitudes between simulated results and observations through statistic parameters. The set of statistic parameters recommended by Hanna et al. (1993) and Borrego et al. (2008), and listed in Table 6.2, are used to evaluate the WRF-EURAD modelling system performance regarding the REF scenario results for PT05 and OP01 domains, bias-corrected through the application of the RAT04 technique (section 6.2).

Measured concentrations from a set of stations of the Portuguese air quality monitoring network (see Figure 6.1 and Table 6.1) were used in the operational evaluation process here presented, regarding CO, NO_2, O_3, PM10 and PM2.5 concentrations. This evaluation process cannot be applied to NMVOC because there are no measurements of total NMVOC on the national monitoring network.

The correlation factor (R) reflects the linear relationship between two variables. However it is insensitive to either an additive or a multiplicative factor. To allows for sensitivity on the difference in observed and predicted values as well as proportionality changes, Elbir (2003) included the Index of Agreement (IA) to the statistical analysis. This indicator determines the degree to which magnitudes and signs of the observed value about mean observed value are related to the predicted deviation about mean predicted value (Borrego et al., 2008). Root Mean Square Error (RMSE) and bias are frequently used measures of the differences between values predicted and the values actually observed (bias) or absolute values (RMSE). Bias reflects the trends of the model results error: a negative bias indicates that the model is overestimating and a positive bias reveals an underestimated trend. However bias should not be analysed alone, because so over-prediction and under-prediction may cancel each other, leading to bias=0, the result for an ideal prediction. On the other hand, RMSE allows assessing the magnitude of these errors (Ribeiro, 2008). Thus, bias and RMSE can provide add value to each other when taken together. Normalised mean square error (NMSE) and RMSE give information about the errors obtained within the observed-predicted pairs of results. However, RMSE ignores the range of the variable, which in some cases could lead to misleading interpretations of this parameter result. Thus, a normalized form of the parameter, NMSE, could be more adequate. The fraction of predictions within a factor of 2 of observations (FAC2) is a tool to remove outliers and can be a way of improving statistical analysis results. Thus, FAC2 is considered as the most robust measure (Borrego et al., 2008; COST Action 732, 2009).

Table 6.2 – Statistical quality indicators for air quality model performance evaluation (Hanna et al., 1993; Borrego et al., 2008).

Indicator	Formula	Range of acceptable values	Ideal value
Correlation coefficient (R)	$R = \frac{\sum_{i=1}^{N}(C_{Oi}-\overline{C_O})(C_{Mi}-\overline{C_M})}{\sqrt{\sum_{i=1}^{N}(C_{Oi}-\overline{C_O})^2(C_{Mi}-\overline{C_M})^2}}$	[0.0 ; 1.0]	1.0
Index of agreement (IA)	$IA = 1 - \frac{\sum_{i=1}^{N}(C_{Mi}-C_{Oi})^2}{\sum_{i=1}^{N}(\lvert C_{Mi}-\overline{C_O}\rvert + \lvert C_{Oi}-\overline{C_O}\rvert)^2}$	[0.0 ; 1.0]	1.0
Root mean squared error (RMSE)	$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(C_{Oi}-C_{Mi})^2}$	n.a.	0.0
Normalized mean squared error (NMSE)	$NMSE = \frac{\overline{(C_O-C_M)^2}}{\overline{C_O C_M}}$	n.a.	0.0
Mean systematic error (bias)	$bias = \frac{1}{N}\sum_{i=1}^{N}(C_{Oi}-C_{Mi})$	n.a.	0.0
Fractional bias (FB)	$FB = \frac{\overline{C_O} - \overline{C_M}}{0{,}5(\overline{C_O}+\overline{C_M})}$	[-2.0 ; 2.0]	0.0
Average normalized absolute bias (ANB)	$ANB = \left(\frac{\lvert C_O - C_M\rvert}{C_O}\right)$	n.a.	0.0
Normalized standard deviation (NSD)	$NSD = \frac{\sigma_M}{\sigma_O}$	[0.0 ; 1.0]	1.0
Geometric mean bias (MG)	$MG = exp\left(\overline{\ln C_O} - \overline{\ln C_M}\right)$	> 0.0	1.0
Geometric variance (VG)	$VG = exp\left[\left(\overline{\ln C_O} - \overline{\ln C_M}\right)^2\right]$	> 0.0	1.0
Factor of two of Observations (FAC2)	$FAC2 = \frac{\sum_{i=1}^{N} A_i}{N}$ $with\ A_i = \begin{cases} 1\ for\ 0.5 \le \frac{C_{Mi}}{C_{Oi}} \le 2.0 \\ 0, else \end{cases}$	n.a.	1.0

n.a. – not applicable.
C_{Oi} and C_{Mi} are the observed and predicted concentration in monitoring station *i* in *n* monitoring station.
$\overline{C_O}$ and $\overline{C_M}$ are the averaged concentration observed and predicted.
σ_O and σ_M are the standard deviation of observations and predictions.

Due to the distributions of the majority of pollutant concentrations are close to log-normal, the linear measures fractional bias (FB) and normalized mean square error (NMSE) may be exceedingly influenced by infrequently occurring high observed and/or predicted concentrations, whereas the logarithmic measures geometric mean bias (MG) and geometric variance (VG) may provide a more balanced treatment of extreme high and low values. Nevertheless, MG and VG may be excessively influenced by extremely low values, near the instrument thresholds and are undefined for zero values. FB and MG are measures of mean relative bias and indicate only systematic errors. NMSE and VG are measures of mean relative scatter reflecting both systematic and unsystematic (random) errors, but they are not a direct measure of these errors (Borrego et al., 2008).

The statistical quality indicators shown in Table 6.2 were adopted as a common European model evaluation framework (Olesen, 2001), which have been integrated and updated into the DELTA tool (Thunis et al., 2012). The DELTA tool is a software developed in the scope of the FAIRMODE (URL 11) activity by the Joint Research Centre of the European Commission for the evaluation and benchmarking of air quality modelling applications and for rapid diagnostics of model performances of air quality models, focusing on O_3, PM10 and NO_2 so far, addressing from local to regional scales. In the coming years, the DELTA tool will be extended to other pollutants mentioned in the air quality Directive (2008/50/EC), as well as for scenarios assessment. In spite of this software is a powerful and updated tool for air quality modelling evaluations, its application in this work was limited since the modelling system evaluation in terms of CO and PM2.5 is required. Thus, the operational evaluation of the WRF-EURAD modelling system was not based on DELTA tool, but on the statistical parameters listed in Table 6.2. The main results from the operational evaluation exercise are presented in section 6.3.1 for mainland Portugal domain (PT05) and in section 0 for the Porto urban area (OP01).

In spite of the results are bias-corrected, analysing their bias values, as well as bias related parameter values, is important to verify how far the systematic error is minimized. This is especially important because RAT04 results may be sharply influenced by high pollutant concentrations due to air pollution episodes or errors on observed and modelled data, and then these errors are propagated through the 4-days period (Borrego et al., 2011).

6.3.1 PT05

Regarding the PT05 simulation domain, the median of the statistic parameters estimated for each type of station environment are presented in Figure 6.3, in order to investigate the main differences on modelling system performance over rural, suburban and urban environments.

As expected, WRF-EURAD modelling system results unbiased (hereinafter referred to as predicted concentrations) exhibit statistical parameters values close to the ideal ones, in particular for background rural stations (Figure 6.3). This was already expected since background influence in rural environments is not largely influenced by anthropogenic emissions, which decrease the uncertainty associated to the simulation processes.

Bias values (Figure 6.3a) are typically negative suggesting that the results from the RAT04 technique application are slightly under predicted for all studied pollutants. However, they are insignificants being smaller than 0.5 μg·m^{-3} (absolute value) for NO_2, O_3, PM10 and PM2.5, and smaller than 1.3 μg·m^{-3} (absolute value) for CO.

High RMSE values (Figure 6.3b) were found for CO in urban (154.3 μg·m^{-3}) and rural (41.8 μg·m^{-3}) environments, but other parameters such as NMSE, FAC2, ANB and NSD (Figure 6.3c,d) suggest that CO is well predicted, which is also translated by the daily profiles in Figure 6.4. This is mainly because the magnitude of the CO concentrations is higher comparing to the other pollutants, fact that NMSE has into account, contrarily to RMSE.

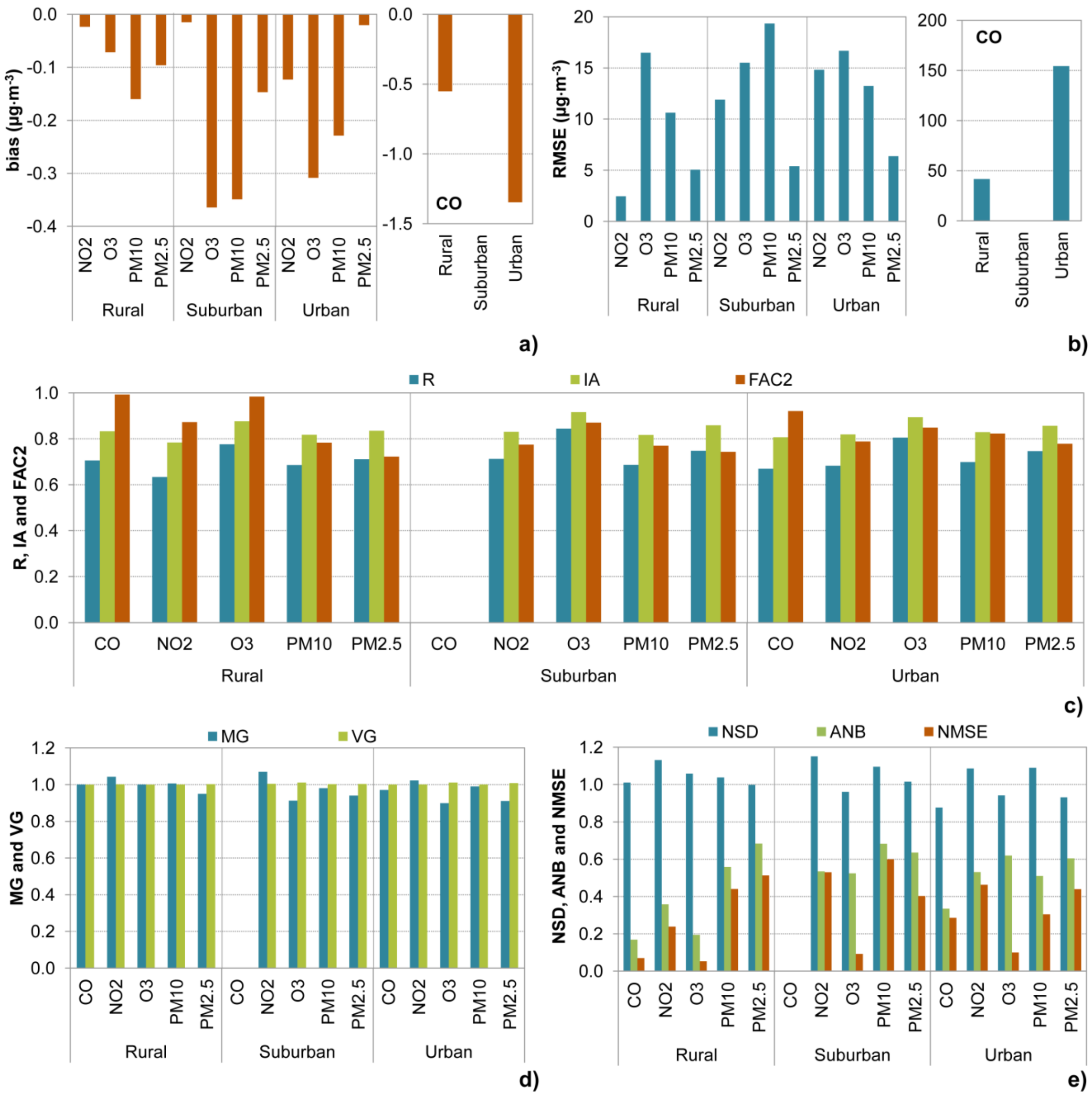


Figure 6.3– Statistical parameters for the corrected (RAT04) results from the WRF-EURAD modelling system, regarding the REF scenario (2012 year), for each pollutant and station environment: a) bias (µg·m^{-3}); b) RMSE (µg·m^{-3}); c) R, IA and FAC2; d) MG and VG; e) NSD, ANB and NMSE. Median for all the monitoring sites, over the PT05 domain.

In Figure 6.4 are compiled a daily profile per studied pollutant and type of environment (rural, suburban and urban), comparing measured and predicted concentrations, including their concentration percentiles 25th/75th. According to the statistical parameters (Figure 6.3) and daily profiles (Figure 6.4), the hourly mean predicted concentrations are quite similar to measured concentrations for all the studied pollutants and for all environments.

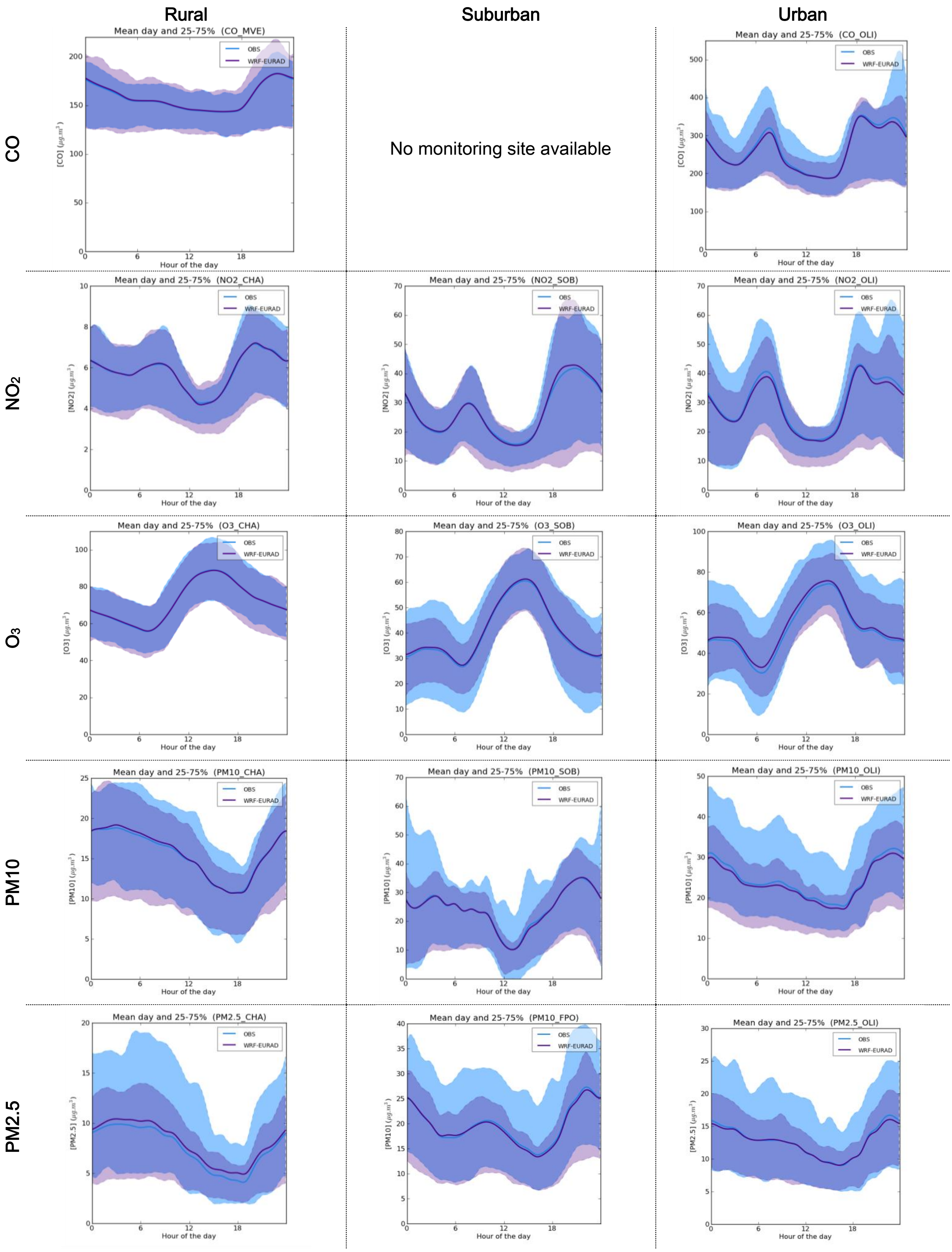


Figure 6.4 – Daily profiles of measured (blue line) and predicted (purple line) concentrations of CO, NO_2, O_3, PM10 and PM2.5, as well as the concentration ranges between percentiles 25th/75th, over the PT05 domain, regarding rural, suburban and urban environments.

For O_3, a secondary pollutant, daily profiles present higher concentrations during the periods of sunlight and higher temperature, while the daily profiles of the remaining pollutants present higher concentrations during the night-time than during the daylight period, in rural environments. This concentrations behaviour is also found for PM10 and PM2.5 in suburban and urban environments. On the other hand, on suburban/urban profiles for CO and NO_2, two pecks can be identified at the typical rush hours (6h - 9h and 17h - 22h). This is mainly due to the importance of the CO and NO_2 emissions from the transport sector in urban/suburban areas.

Despites the good quality of the predicted results, presenting identical daily profiles between measured and predicted concentrations, the daily profiles of the percentiles 25th/75th, regarding the measured concentrations, typically cover a wider range of concentrations than for predicted data (Figure 6.4). This is especially visible for PM10 and PM2.5, which the daily profiles of the 75th percentile of the predictions are lower than those measured, while the daily profiles of the 25th percentile of measured and predicted concentrations are similar. This suggests that emissions of these pollutants used as input data to WRF-EURAD simulations may be underpredicted.

6.3.2 OP01

The OP01 domain, covering the Porto urban area, comprises 8 monitoring stations under urban and suburban environments (Table 6.1). Moreover, because this is an area strongly influenced by industrial and traffic activities, the evaluation process will take into account monitoring stations with industrial and traffic influence, in addition to the background. In this sense, the median values of the statistical parameters estimated per type of station influence are presented in Figure 6.5. Note that there are no rural monitoring stations in this domain (Table 6.1).

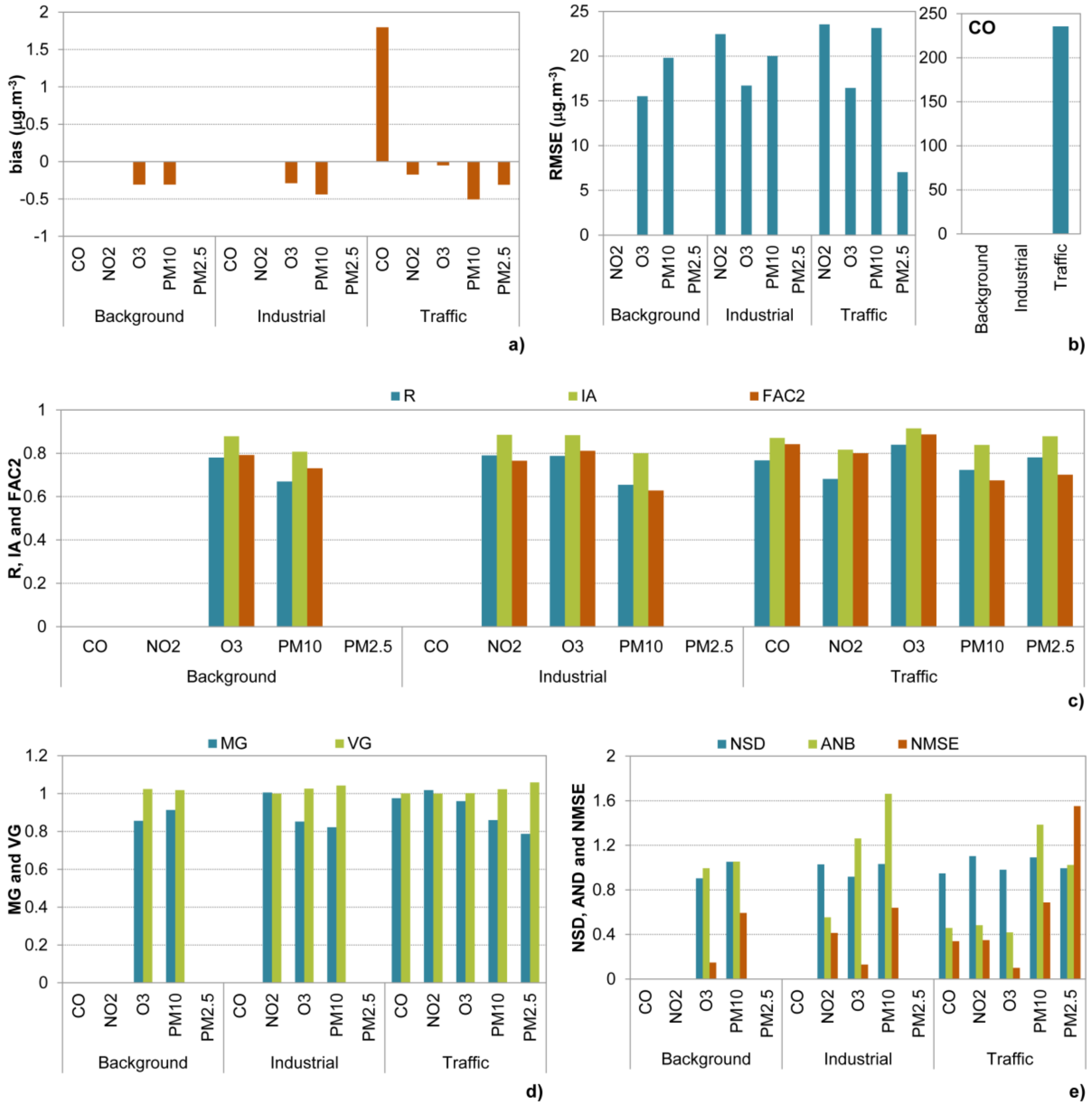


Figure 6.5 - Statistical parameters for the corrected (RAT04) results from the WRF-EURAD modelling system, regarding the REF scenario (2012 year), for each pollutant and station environment: a) bias (µg·m⁻³); b) RMSE (µg·m⁻³); c) R, IA and FAC2; d) MG and VG; e) NSD, ANB and NMSE. Median for all the monitoring sites, over the OP01 domain.

Similarly to what was found for the previous domain (PT05, section 6.3.1), the statistical parameters estimated are close to the ideal values (Figure 6.5) presenting similar magnitudes than for PT05. The main reason to explain this is related to the bias-correction technique applied to the raw prediction results from WRF-EURAD modelling system for both domains.

As well as verified to PT05, the RMSE regarding CO concentrations is about ten times larger than for other pollutants, due to its high magnitude of concentrations values. On the other hand, for the OP01 domain there is no clear evidence that the predicted results have more quality for sites with background influence than for others, since the majority of the statistical parameters have similar values regardless the pollutant and the monitoring site influence.

The daily profiles, comparing measured and predicted concentrations as well as their 25th/75th concentration percentiles, for each pollutant and type of influence (background, industrial and traffic) are presented in Figure 6.6. The analysis of these daily profiles corroborates the good overall performance of the air quality modelling, predicting the hourly mean concentration of the several pollutants over the OP01 domain. The PBL height variation during the day and the emission time-profiles (Figure 5.5) are also reflected by daily profiles.

Observed and predicted 25th/75th percentile profiles (Figure 6.6) are close to each other, while in PT05 (Figure 6.4) only the predicted 25th percentile match to observations, suggesting that the improvement on road traffic emissions in terms of spatial resolution performed and described in Chapter 4 should be taking into account in further simulations for 1 × 1km^2 but also for 5 × 5 km^2 horizontal resolutions.

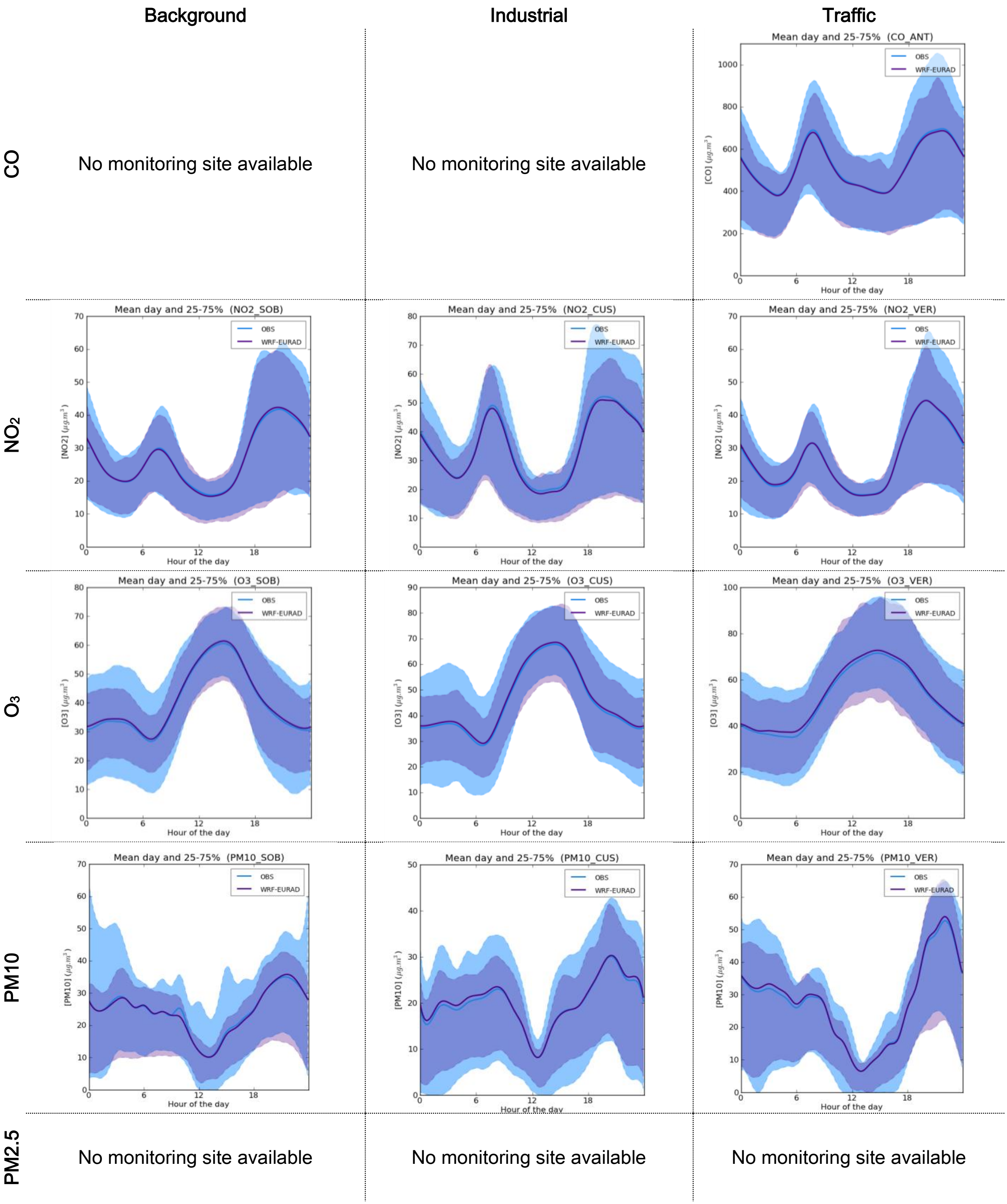


Figure 6.6 – Daily profiles of measured (blue line) and predicted (purple line) concentrations of CO, NO_2, O_3, PM10 and PM2.5, as well as the concentration ranges between percentiles 25th/75th, over the OP01 domain, regarding background, industrial and traffic influence.

Chapter 7. Impacts of biodiesel use on air quality

The impacts of biodiesel use on air quality over mainland Portugal and the Porto urban area are addressed and discussed in this chapter. The emission scenarios REF and B20, developed in section Chapter 4, were used as input data to the WRF-EURAD modelling system (Chapter 5), which performance evaluation is addressed in Chapter 6, in order evaluate eventual impacts due to the use of B20 fuel instead of pure petroleum-based diesel in road transports. The analysis presented here is focused on mean concentration differentials (B20-REF) of CO, NO_2, NMVOC, O_3, PM10 and PM2.5, for three different periods defined in accordance to the European Directive 2008/50/EC on ambient air quality and cleaner air for Europe, in the scope of air quality assessment:

- Annual: The entire year of 2012;
- Summer season: from April to September 2012;
- Winter season: from January to March and from October to December 2012.

7.1 Impacts on air quality over mainland Portugal

The REF and B20 emission scenarios defined in Chapter 4 were used to simulate the air quality over mainland Portugal (PT05), through the application of the WRF-EURAD mesoscale numerical modelling system (Chapter 5). The main results are shown in Figure 7.1 regarding the spatial distribution for annual-, summer- and winter-mean concentrations of NO_2, NMVOC and O_3 for the REF scenario. The differentials found between both scenarios (B20-REF) are also presenting in Figure 7.1. NO_2 and O_3 concentration values are presented in $\mu g \cdot m^{-3}$. However, due to the multiple compounds in the NMVOC its concentrations are in parts per billion in volume basis (ppbv).

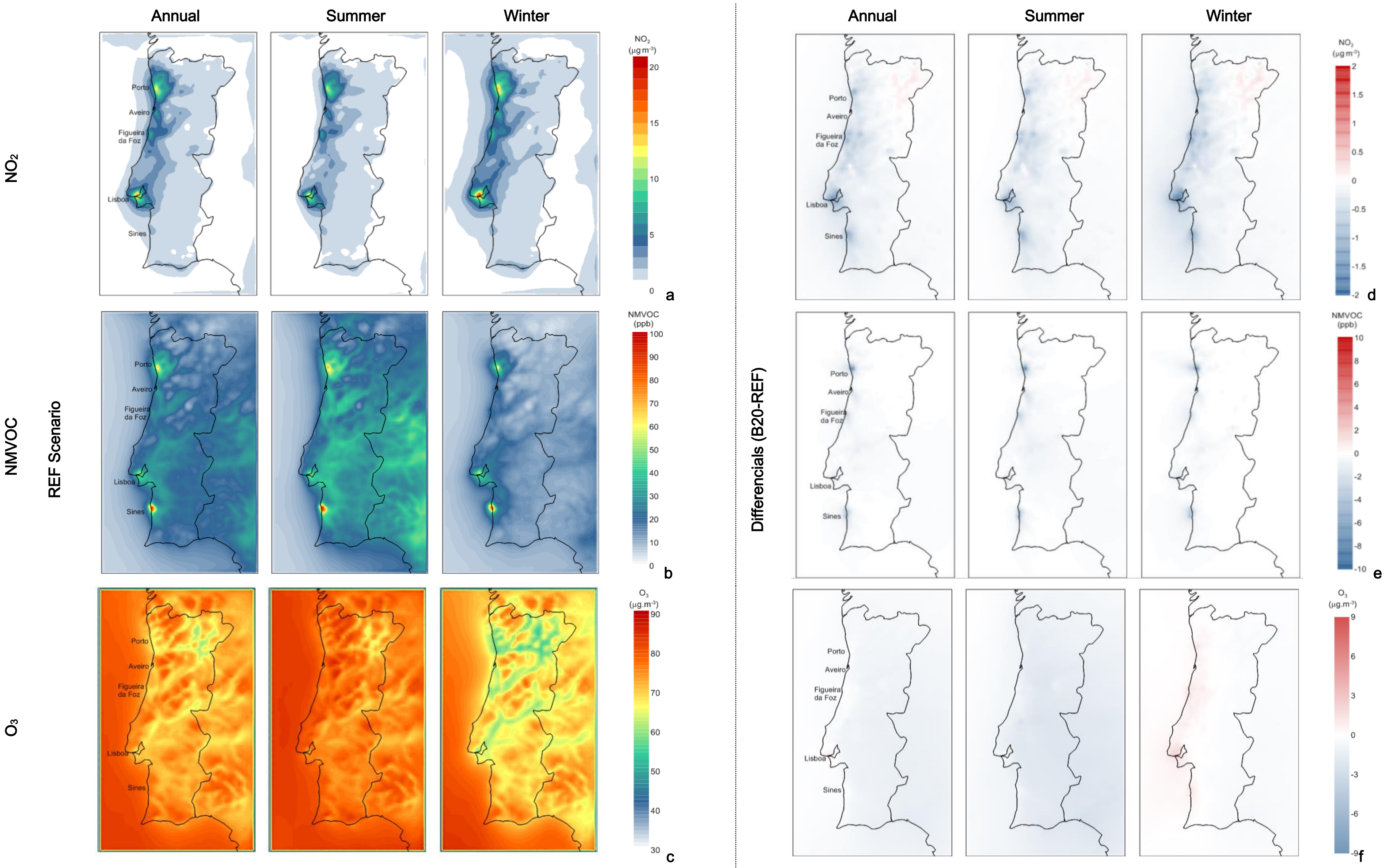


Figure 7.1 – Annual, summer and winter mean concentrations of NO_2 (µg·m^{-3}), NMVOC (ppbv) and O_3 (µg·m^{-3}) for REF scenario (a-c) and differential concentrations between B20 and REF (d-f), over the PT05 domain.

In general, the simulation results (Figure 7.1) show that the use of B20 fuels may implies a reduction on air quality levels in terms of NO_2 and NMVOC, especially in urban areas. In spite of NOx total emissions increase in about 3% with B20 use (Figure 4.7), NO_2 concentrations decrease over the West coast of Portugal, representing a reduction in order of ~2 μg·m^{-3} in Lisbon and ~1 μg·m^{-3} in Porto urban areas (Figure 7.1a). In fact, relations between NOx emissions and NO_2 concentrations are driven by complex nonlinear chemistry mechanisms, which also include NMVOC and ozone. This illustrates the importance of the use of a chemical transport model, like EURAD-CTM, to investigate the impacts on air quality in the scope of emission scenarios.

The simulation results for REF scenario (Figure 7.1a) also suggest that NO_2 concentrations are superior during the winter period then in the summer, presenting higher reductions of this pollutant concentrations when B20 is compared to REF scenarios. This leads to a slight increment of the O_3 average concentration (Figure 7.1c) in about 1-2 μg·m^{-3} over the West coast, especially in urban regions.

In the summer season, O_3 concentrations decrease about 1.5 μg·m^{-3} over the inland of the territory, representing less than 2% of the total O_3 concentrations. Negligible changes are found in the most polluted areas in terms of NO_2 and NMVOC (Lisbon, Porto, Aveiro, Sines and Figueira da Foz regions).

NMVOC is a group of pollutants mainly emitted by biogenic activity (especially during the summer, as shown in Figure 7.1b) and solvent industries, such as petroleum refineries located in Sines and Matosinhos (close to Porto). According to INERPA (APA, 2011), the transport sector is responsible by 3.5% of the NMVOC total emissions and the use of B20 instead of pure diesel in road traffic can reduce NMVOC emissions in about 2%, as already discussed in section 4.4 (Figure 4.7). This emission reduction induces a decrease on NMVOC concentrations in about 8 ppbv over Porto and Sines regions. The simulation results also suggest that the use of B20 fuel will contribute to reduce NMVOC in a maximum of 5 ppbv over the remaining territory. Still for NMVOC, no significant changes on B20-REF differentials were also verified when summer is compared to winter period results over the West coast, which is the national area mostly influenced by traffic activities.

To investigate the variations on the concentration bins, an analysis through histograms was carried out. Figure 7.2 presents the histograms for B20 and REF regarding NO_2, NMVOC and O_3, for annual, summer and winter periods. This figure also depicts the difference between the probability of occurrence of B20 against REF, for each concentration bin ($\Delta P_{B20-REF} = P_{B20_{bin\,i}} - P_{REF_{bin\,i}}$).

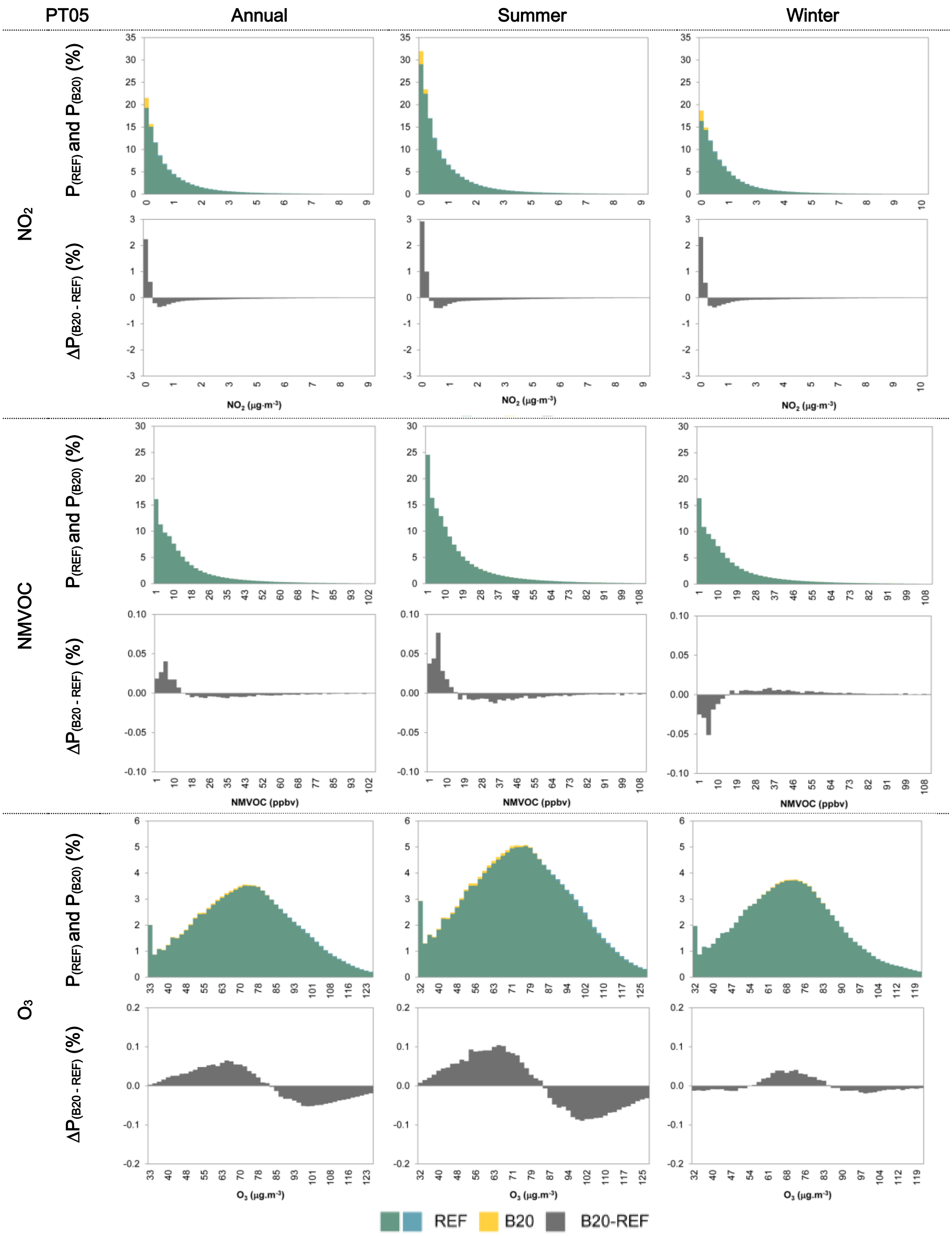


Figure 7.2 – Histograms of 1-99% of NO_2 (top), NMVOC (middle) and O_3 (bottom) hourly concentrations, regarding annual, summer and winter periods for REF (blue or green) and B20 (yellow) scenarios, for the PT05 domain. The difference between the probabilities of occurrence of B20 against REF is presented in grey.

In general, the histograms reveal that the lowest concentrations have higher probability of occurrence in B20 scenario comparing to REF. For NO_2 and NMVOC, variations between B20 and REF are progressively less significant with the increase of concentration magnitude. Regarding ozone, the turning points on $\Delta P_{(B20\text{-}REF)}$ are close to the concentration peaks for annual and summer periods. However, this is not verified for the winter period (Figure 7.2) mainly due to the O_3 concentration increasing over West coast, as verified in Figure 7.1 and discussed above. For this case, only the concentration range with higher probability of occurrence (55 – 83 $\mu g \cdot m^{-3}$) will increase when road traffic is fuelled with B20.

The spatial distribution of annual-, summer- and winter-mean concentrations of CO, PM10 and PM2.5 are presented in Figure 7.3, as well as their spatial differential between B20 and REF scenarios. Among these pollutants, CO is the most relevant one, with road traffic activities being responsible by 36% of the total CO emissions in Portugal, while PM10 and PM2.5 road traffic emissions represent about 5% of the total emissions of these pollutants (APA, 2011). The air quality simulation results (Figure 7.3) reveal that the reduction in almost 20% of the CO emissions (Figure 4.7), by the use of B20 fuels, can improve air quality levels over the West coast: CO concentrations may reduce in about 20-25% in Lisbon and 17-22% in Porto urban areas (Figure 7.3d). Despites CO concentrations are typically higher during the winter months in comparison to the summertime (Figure 7.3a), the differentials between scenarios and season are not evident (Figure 7.3d).

Regarding PM10 and PM2.5 (Figure 7.3b-c,e-f), the simulation results suggest that the use of B20 fuels leads to a no significant decrease of these pollutant concentrations over mainland Portugal (Figure 7.3e-f). Over both urban areas of Lisbon and Porto, but also on Aveiro and Figueira da Foz, where concentration reductions are higher, variations on PM concentrations do not exceed 0.08 $\mu g \cdot m^{-3}$, representing a reduction by 0.2% of these current pollutant concentrations.

Figure 7.4 shows the histograms of the CO, PM10 and PM2.5 hourly-based concentrations (percentiles 1-99%) regarding the PT05 simulation domain, for both scenarios and the differentials between them ($\Delta P_{B20-REF} = P_{B20_{bin\,i}} - P_{REF_{bin\,i}}$).

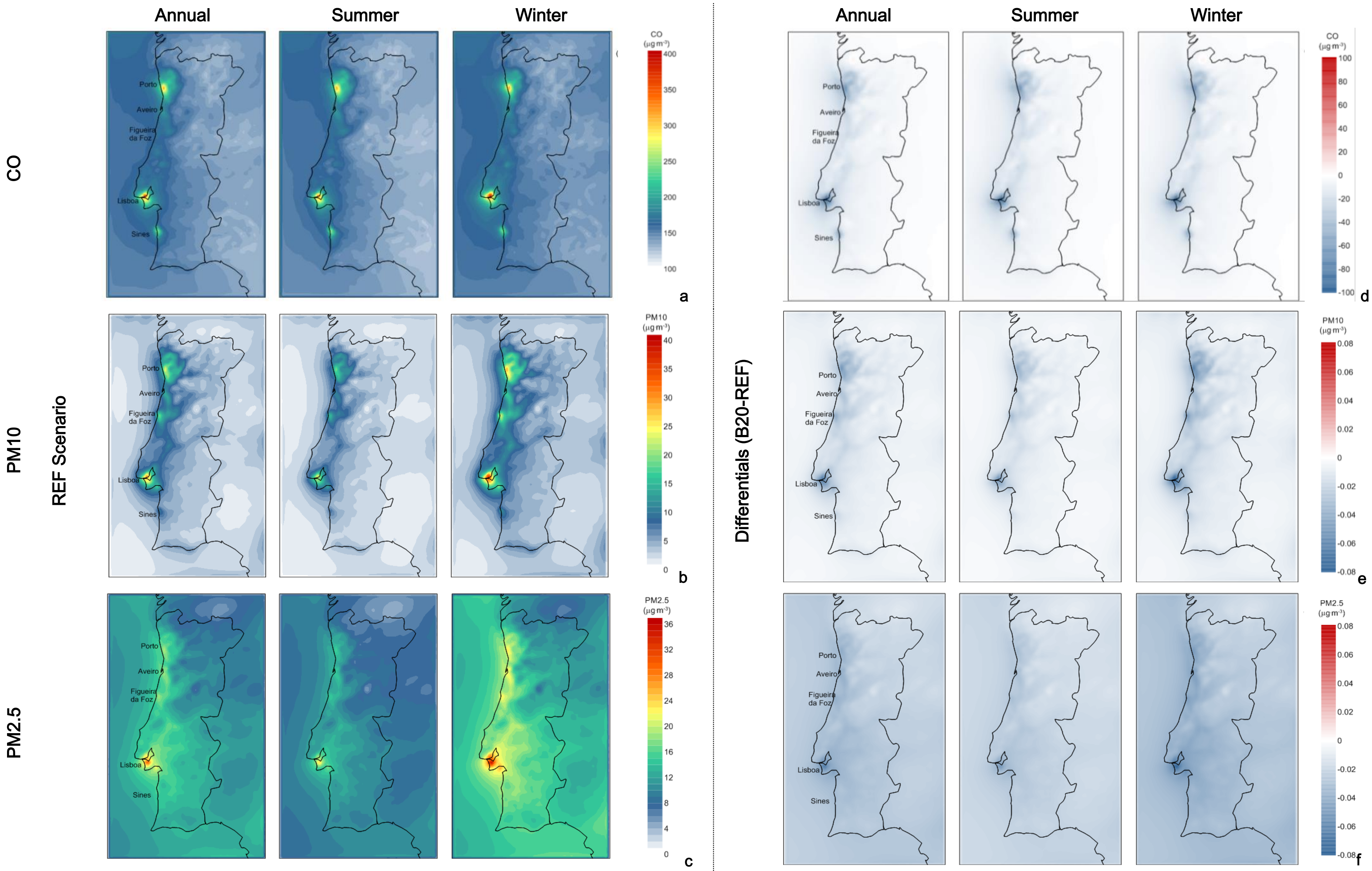


Figure 7.3 - Annual, summer and winter mean concentrations of CO, PM10 and PM2.5 for REF scenario (a-c) and differential concentrations between B20 and REF (d-e), over the PT05 domain.

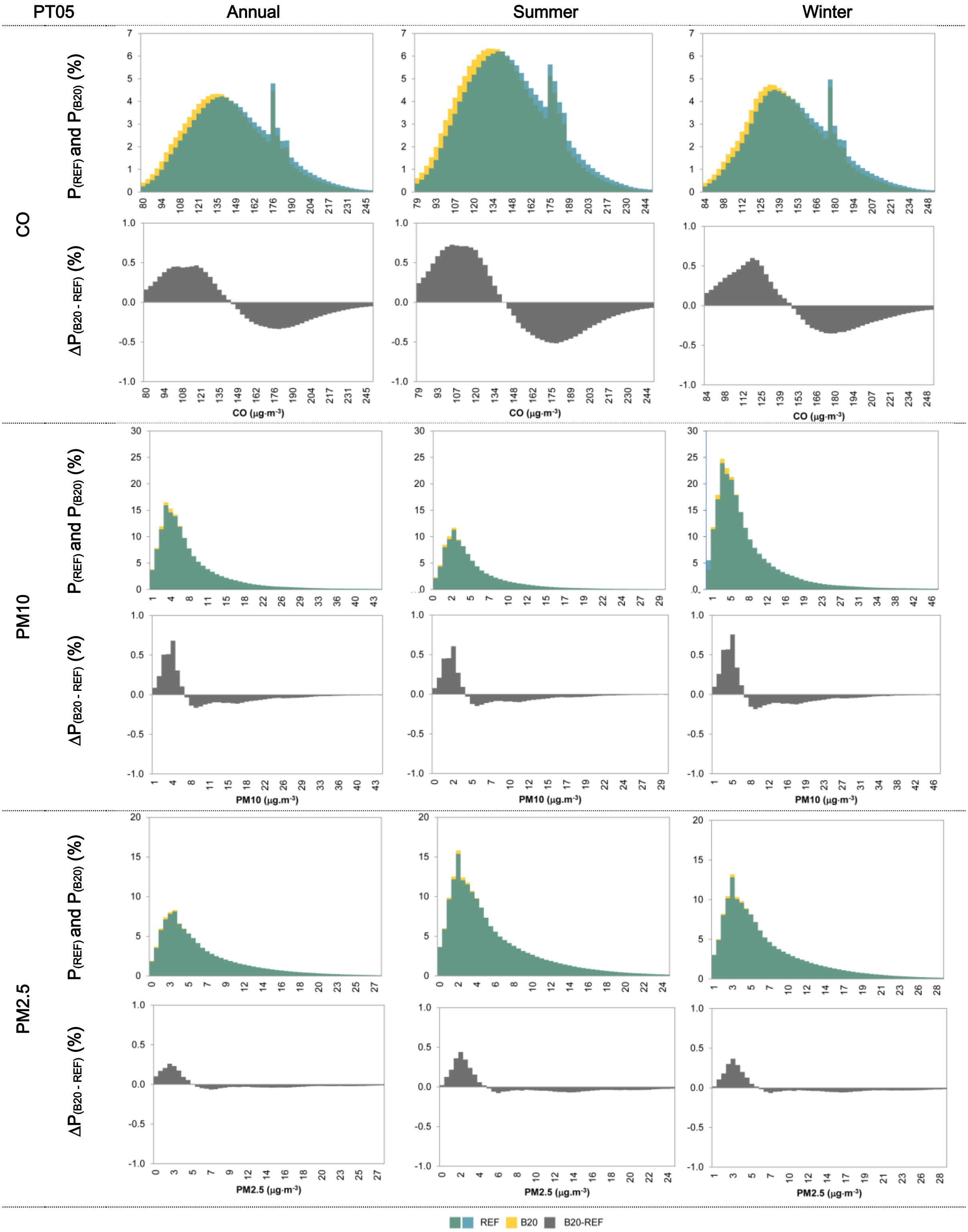


Figure 7.4 – Histograms of 1-99% of CO (top), PM10 (middle) and PM2.5 (bottom) hourly concentrations, regarding annual, summer and winter periods for REF (blue or green) and B20 (yellow) scenarios, for the PT05 domain. The difference between the probabilities of occurrence of B20 against REF is presented in grey.

The graphs in Figure 7.4 suggest that the use of B20 fuels increase the probability of occurrence of the lowest CO concentrations (from ~80 to ~135 $\mu g \cdot m^{-3}$) and a reduction on the probability for concentrations after the peak of the distribution curve. Additionally, a second probability peak is notable for concentrations around 175 – 190 $\mu g \cdot m^{-3}$, suggesting that these peaks, that represent the CO concentrations in urban areas, will be reduced in B20 scenario.

Regarding PM histograms, they suggest that the B20 scenario increases the probability of occurrence of the concentrations up to 8 and 5 $\mu g \cdot m^{-3}$ for PM10 and PM2.5, respectively. For higher concentrations the results suggest that B20 induce a reduction on their probability of occurrence.

In sum, the use of a B20 to fuel road transports can contribute to an improvement of NO_2 and CO concentration levels in urban airshed in order of 10 and 30%, respectively. A no significant increase (~2%) was found to O_3 winter-mean concentrations over the entire West coast of mainland Portugal. For the remaining studied pollutants, namely PM10 and PM2.5, their mean concentrations will be reduced all over the territory, however in a no significant amount (<1%).

7.2 Impacts on air quality in Porto urban area

To investigate more deeply the influence of B20 fuels used by road transports in urban areas, a downscaling modelling technique was performed over the Porto urban area (OP01 domain) using the WRF-EURAD mesoscale modelling system to simulate REF and B20 scenarios (see section Chapter 4) with higher resolution. The OP01 simulation domain has a horizontal resolution of 1×1km^2 and covers an area of 26 × 26 km^2 (Table 5.2).

The spatial distribution of annual-, summer- and winter-mean concentrations of NO_2, NMVOC and O_3 obtained for the REF scenario, as well as spatial distribution of differential of those pollutant concentrations between both scenarios is presented in Figure 7.5.

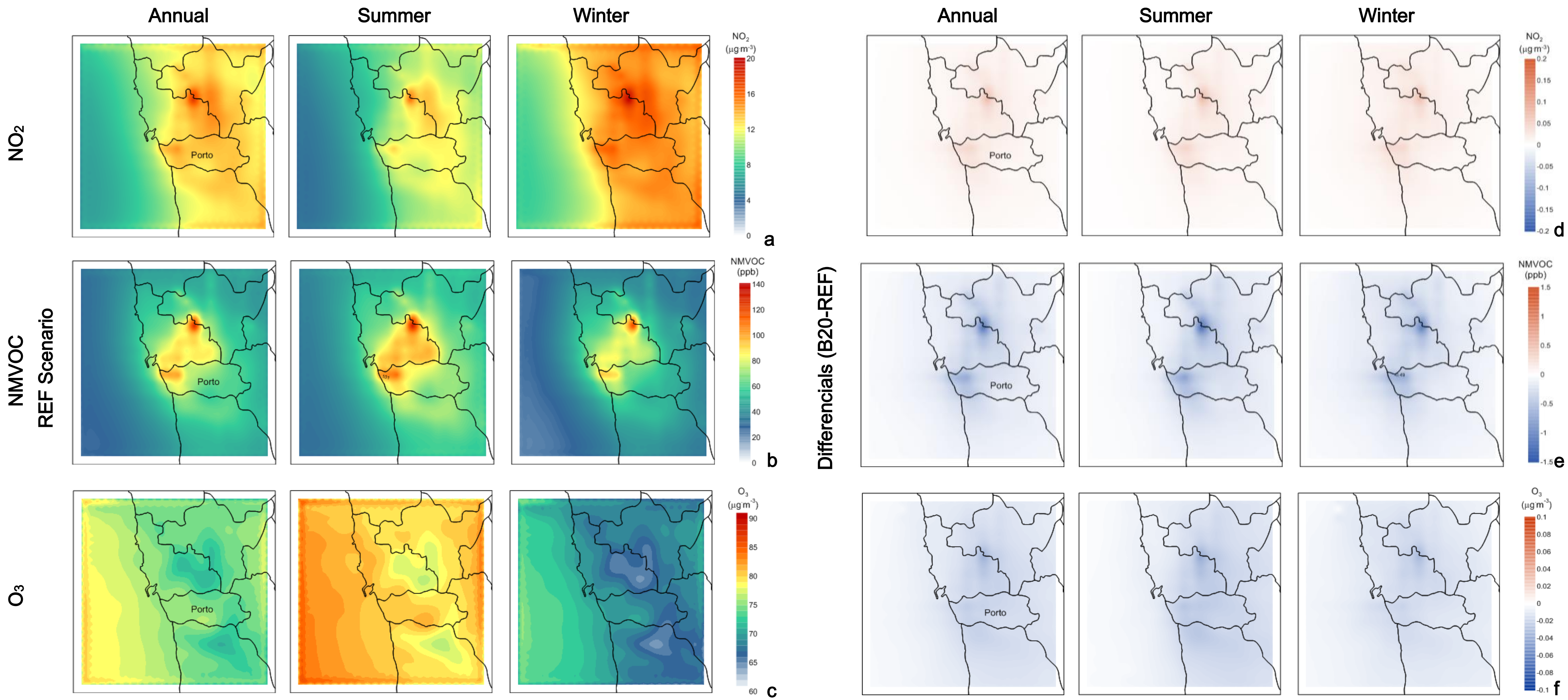


Figure 7.5 – Annual, summer and winter mean concentrations of NO_2 ($\mu g \cdot m^{-3}$), NMVOC (ppbv) and O_3 ($\mu g \cdot m^{-3}$) for REF scenario (a-c) and differential concentrations between B20 and REF (d-f), over the OP01 domain.

The simulation results presented in Figure 7.5 suggest that NMVOC and O_3 concentrations decrease over the OP01 when B20 fuel is used instead of pure diesel. On the other hand, an increase of NO_2 concentrations was predicted, regardless the period of the year. Nevertheless, these variations on NO_2, NMVOC and O_3 concentrations are very small reaching the maximum of 0.07 $\mu g{\cdot}m^{-3}$ for NO_2 and -0.9 ppbv for NMVOC in the winter, and -0.03 $\mu g{\cdot}m^{-3}$ for O_3 during the summer period. Variations found for O_3 were in order of 0.05%, which may be considered as negligible. This was expected because ozone is mainly formed during the transport of its precursors emitted in urban areas (namely, NO_2, NMVOC and CO), causing ozone formation in remote regions. Also, the small dimension of the OP01 domain (26 $\times$ 26 km^2) may have contributed to the no significant differences found since the transport of ozone precursors may be not completely reproduced.

The areas with largest NO_2 and NMVOC concentration values are Northern and West of Porto city town, matching with major road traffic activity hotspots (Figure 4.3) and higher atmospheric pollutant emission associated (Figure 4.6 and Figure 4.9). As expected, the highest concentration variations, notwithstanding small (less than 1%), are also located in those hotspots.

The histograms of hourly-based concentrations for these three pollutants, which are compiled in Figure 7.6, suggest that the differences between the probabilities of the concentration bins (Figure 7.6, graph in grey) of each scenario are negligible. However, due to the verified increase on NO_2 concentrations for B20 when compared to REF scenario, the histograms reveal that the probability of occurrence NO_2 concentrations between [0 ; 4] $\mu g{\cdot}m^{-3}$ decrease in B20 scenario in order of 0.004%, regardless the season of the year. The opposite is verified to NMVOC, for which the probability of occurrence low concentrations (from 2 to ~40 ppb) increase by 0.02% when B20 is compared to REF scenario. In contrast to PT05, the turning point location of O_3 concentrations is not obvious, especially for the summer period. Nevertheless, for annual and winter periods, there is a trend to increase the probability in the first half of each graph that present ΔP (grey graph in Figure 7.6), which turns to a decreasing trend in the second half of them.

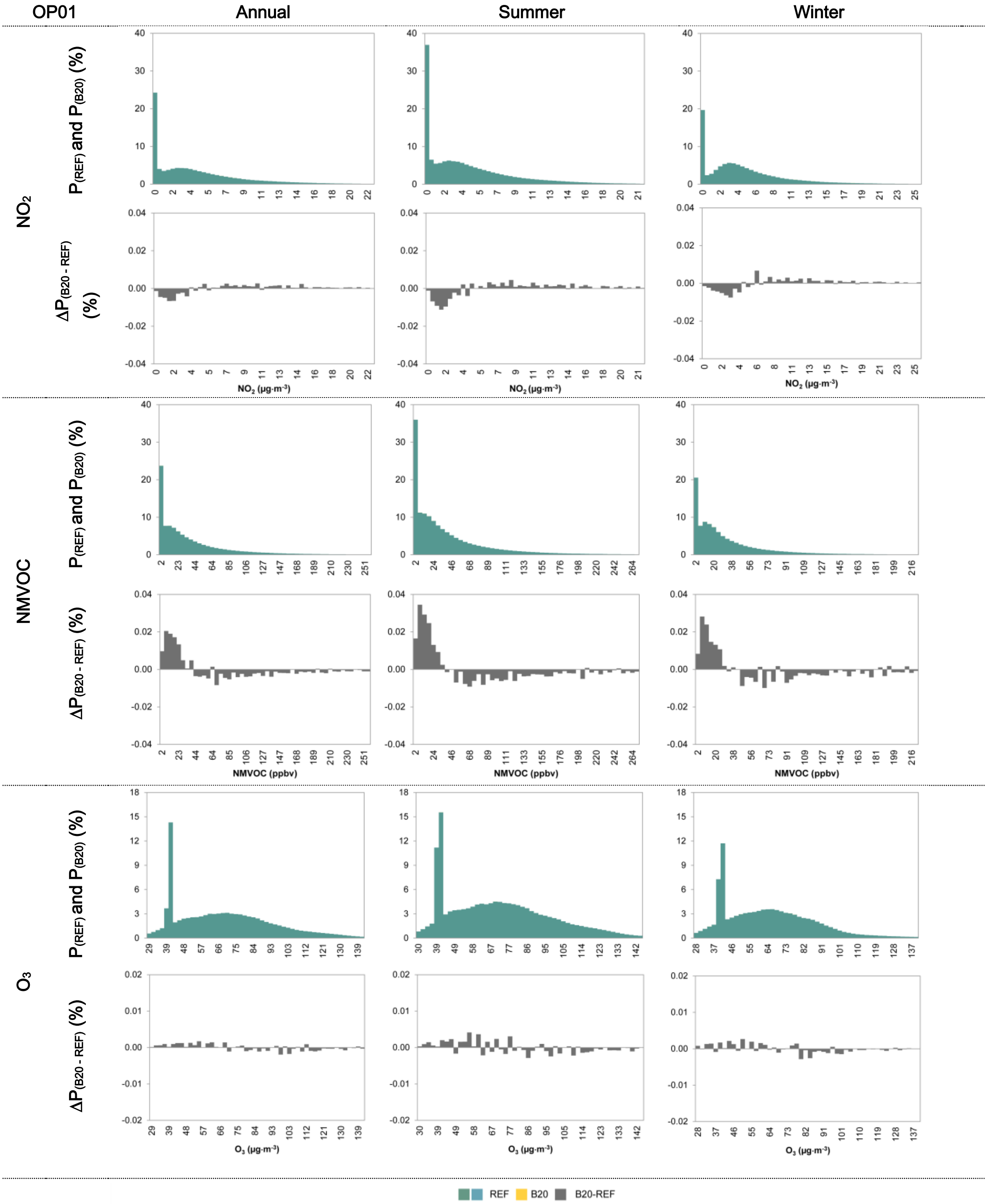


Figure 7.6 - Histograms of 1-99% of NO_2 (top), NMVOC (middle) and O_3 (bottom) hourly concentrations, regarding annual, summer and winter periods for REF (blue or green) and B20 (yellow) scenarios, for the OP01 domain. The difference between the probabilities of occurrence of B20 against REF is presented in grey.

The spatial distribution of annual-, summer- and winter-mean concentration of CO, PM10 and PM2.5 are shown in Figure 7.7, as well as their concentration differentials (B20-REF).

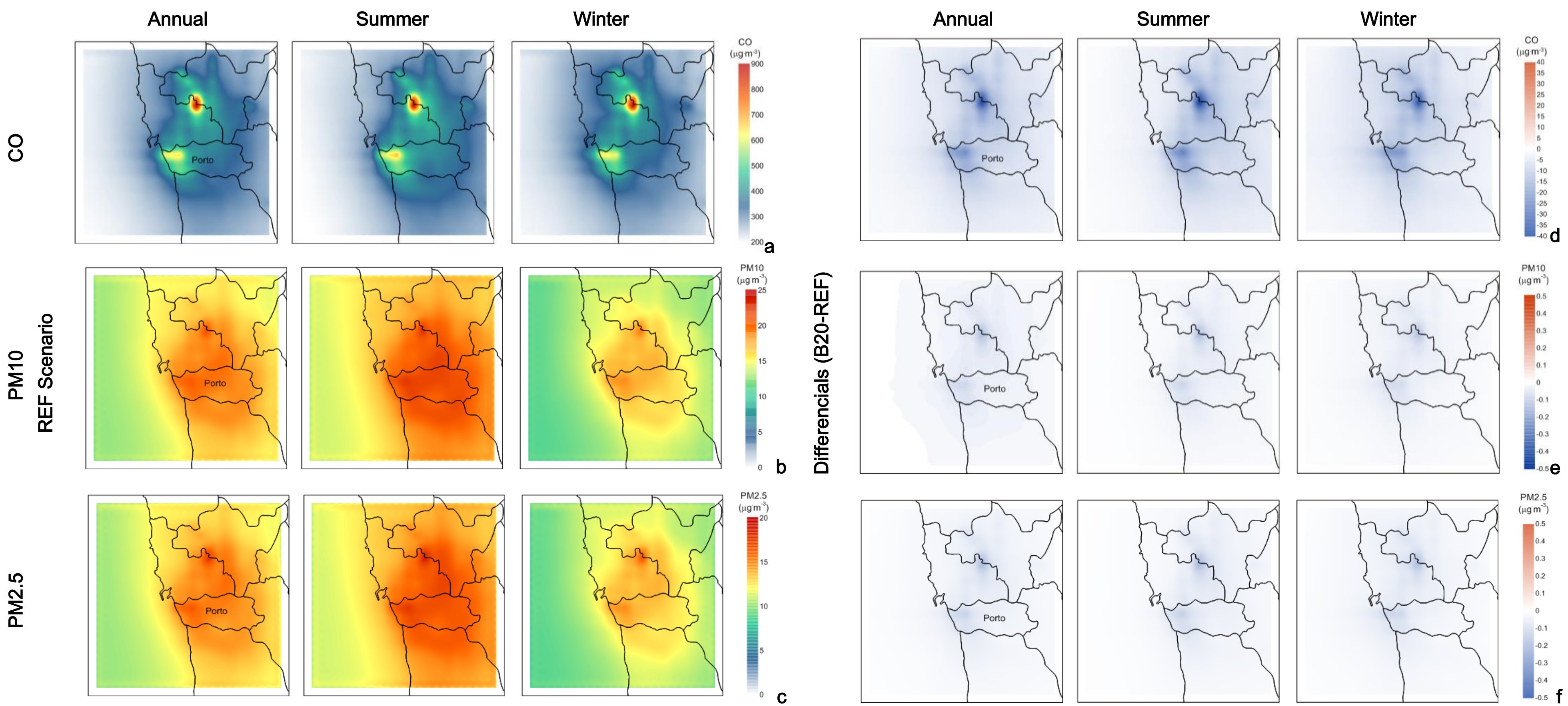


Figure 7.7 – Annual, summer and winter mean concentrations of CO, PM10 and PM2.5 for REF scenario (a-c) and differential concentrations between B20 and REF (d-f), over the OP01 domain.

According to the obtained results (Figure 7.7a), the use of B20 fuel improve CO levels by 5%, reaching a reduction of more than 30 $\mu g \cdot m^{-3}$ on the Northeast hotspots (Figure 7.7). Regarding PM (PM10 and PM2.5), B20 scenario presents lower particulate matter concentrations than REF. Additionally, higher reductions on PM mean-concentrations were found for OP01 (~2%) than for PT05 over the Porto region (~0.2%), suggesting that considering line sources emission, instead of traffic emissions in area, increase the influence of road traffic activities in urban areas.

As verified to NO_2, NMVOC and O_3, also for CO, PM10 and PM2.5. no significant differences were found between B20 and REF scenarios, taking into account the time periods, regarding CO, PM10 and PM2.5. This is verified not only in terms of spatial distribution but also on probability distribution, as shown in the histograms in Figure 7.8. Since the concentrations of these pollutants decrease with the use of B20 instead of pure diesel, the probability of occurrence lower concentrations increase in B20 scenario and decrease for higher concentrations. The turning points for CO, PM10 and PM2.5 correspond to ~270 $\mu g \cdot m^{-3}$, ~12 $\mu g \cdot m^{-3}$ and ~10 $\mu g \cdot m^{-3}$, respectively, which are higher when compared to the turning points verified to the PT05 domain (Figure 7.4): ~145 $\mu g \cdot m^{-3}$ for CO, ~5 $\mu g \cdot m^{-3}$ for both PM10 and PM2.5. This also supports the idea that the simulated influence of road traffic activity on the Porto region is higher when using the OP01 instead of the PT05 simulation domain.

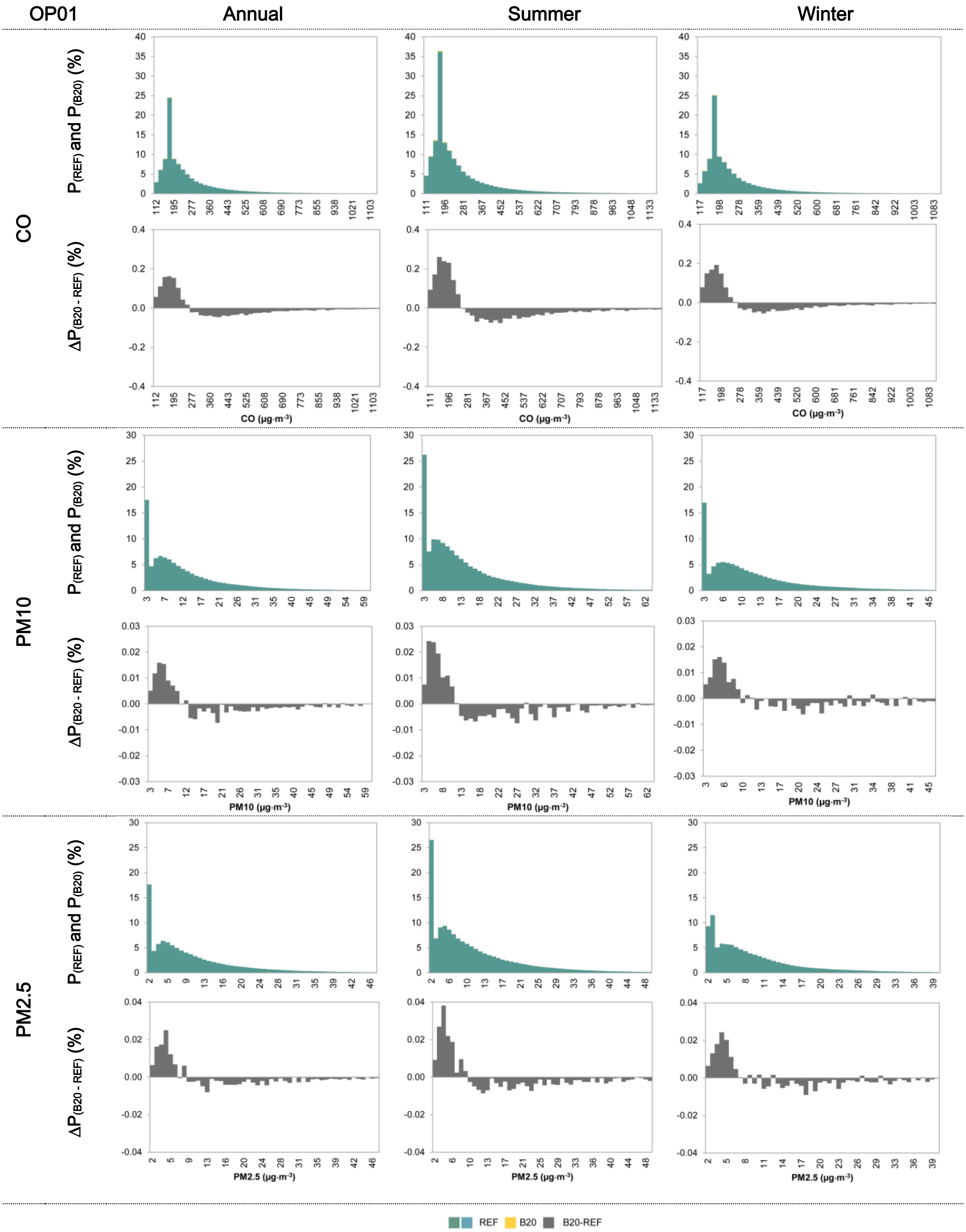


Figure 7.8 - Histograms of 1-99% of CO (top), PM10 (middle) and PM2.5 (bottom) hourly concentrations, regarding annual, summer and winter periods for REF (blue or green) and B20 (yellow) scenarios, for the OP01 domain. The difference between the probabilities of occurrence of B20 against REF is presented in grey.

The graphs representing ΔP for all the studied pollutants regarding the OP01 domain (Figure 7.6 and Figure 7.8), suggest a variability on close concentration bins that is not verified on the PT05 domain (Figure 7.2 and Figure 7.4). This may be caused by unsteady on the modelling system response within the emission scenarios, as a consequence of the high horizontal resolution of the OP01 domain that could be too high for a mesoscale modelling system. The small dimension of the domain can also contributes to the verified unsteady due to a strong influence of the boundary conditions over the entire domain. Even so, this study also allows concluding that the use of high resolution emissions is crucial to obtain more realistic simulations of the urban airshed, which is also foreseen by the modelling system performance evaluation (Chapter 6).

In sum, this analysis confirms that the use of B20 has a small effect on the air quality of the Porto urban area when compared to the REF scenario. Nevertheless, B20 can promote a slight improvement on air quality levels over the OP01 domain especially taking into account CO, but also total NMVOC, PM10 and PM2.5 concentrations. On the other hand, it was predicted that NO_2 concentrations may increase over the entire domain.

Chapter 8. Conclusions

The main aim of this study was to assess the impacts of the use of biodiesel for road traffic on air quality over mainland Portugal and the Porto urban area, through a mesoscale numerical modelling tool. The work is organized in eight chapters, starting with the overall introduction to the scope of this work – climate and energy policies, atmospheric pollutant emissions from the use of biodiesel on road transports and air quality numerical modelling tools.

An overview on the World's biofuels situation is reported with a special focus on the Portuguese biodiesel supply chain. In fact, biofuels have attracted great attention all over the world since 1970's due to their renewability and availability, promising to contribute to regional and rural development as well as to face issues such as climate change, energy external dependence and increasing demand of fossil-fuels. The biofuel mostly produced and consumed worldwide (mainly in America continent) is bioethanol, replacing gasoline. On the other hand, Europe is the greatest producer and consumer of biodiesel as substitute of conventional diesel, which is the main fuel used in the transport sector in European countries, including Portugal.

Based on EU strategies on energy and environmental issues, Portugal started to produce biodiesel derived from energy crops (sunflower, rapeseed, soybean and palm oil) in 2006. Currently, the diesel fuel supplied to the national distribution network has a biodiesel content of 7% (v/v) (B7), being totally produced within the five production plants in mainland Portugal representing 550 kton·y^{-1} of production capacity. In spite of biodiesel production being a driver for economic growth of Portugal, the national biodiesel supply chain has problems of sustainability (only 4% of the total biodiesel consumed in Portugal is certified as sustainable), mainly due to its external dependence on raw materials (rapeseed, soybean and palm oil) that are all imported from Brazil, Malaysia, Indonesia and Romania. Additionally, these energy crops still compete to food feedstocks production.

The sale of blend fuels with more than 7% (v/v) of biodiesel is not allowed in Europe due to a claimed incompatibility of diesel passenger cars for biodiesel blends higher than B7, mainly related to variations on fuel injection characteristics. However, in order to accomplish the goal concerning the replacement of 10% fossil fuels by biofuels in the transport sector in Portugal, the blend fuel would contain about 13% (v/v) of biodiesel, which will probably increase to 20% in a near future, taking into account the importance and the increasing trend of diesel use in Portugal, and assuming a contribution of 2.5% of bioethanol. This demonstrates that there is an inconsistency on transport biofuels policy in Portugal.

An extended literature review on the effects on atmospheric pollutant emissions from the use of diesel/biodiesel blends on road transport was addressed, aiming to identify emission factor to further emission scenarios definition. The majority of the experimental studies suggest that a blend fuel with 20% (v/v) of biodiesel promotes higher combustion efficiency, lower PM, CO and total NMVOC but higher NOx emissions than diesel and other blends. The oxygen content on biodiesel molecule and its higher cetane number have been the most important factors pointed out to explain these improvements as well as to justify increases of aldehyde emissions, such as formaldehyde, acetaldehyde and acrolein. These results are in contradiction with the European guideline that limits to 7% (v/v) the biodiesel content. The increase of carbonyl compounds emissions when biodiesel is used is an issue of concern due to their potential for ozone formation and their carcinogenic characteristics. On the other hand, experimental studies have pointed out that the use of blend fuels reduce aromatic and PAH compound emissions with regards to diesel, especially toluene and xylene.

Besides the influence of the physics and chemical characteristics of the fuel on exhaust gases emissions, it is well known that emissions vary with the vehicle technology and driving characteristics, namely the speed and engine load. Thus, only those studies carried out under European driving cycles were taken in consideration to emission scenarios design. Both the New European Driving Cycle (NEDC) and the Common Artemis Driving Cycle (CADC) comprise different driving cycles covering low to high speeds and engine loads. However, the existing experimental studies are focused on up to EURO 4 light passenger vehicles, not comprising the EURO 5 vehicles built from 2009 to 2014. To overcome this lack of information, an experimental work was conducted aiming the study of exhaust gases emissions from EURO 5 engine operating over the NEDC and fuelled by: pure conventional diesel (B0), B7 and B20. The results of this work suggested that B20 blends revealed an improvement on combustion efficiency when compared to other fuels tested, increasing CO_2 and total VOC emissions and reducing NOx, PM, VOC and CO emissions. This experimental study was also first one in literature presenting results from B7 blend. However, B7 had an unpredictable behaviour presenting large deviation results for all the studied pollutants, pointing out to instability on combustion and catalyst processes, increasing the fuel consumption and emission of all studied atmospheric pollutant. The main reason pointed out to explain such instability is the biodiesel content, since other studies have revealed that a blend with less than 10% (v/v) of biodiesel can promote instability on combustion processes. Additionally, a set of VOC species was analysed, allowing to verify a discrepancy regarding the dominant species among B0, B7 and B20 fuels and revealing that benzene, toluene and octane emissions (dominant VOC on B0 exhaust gases) may decrease between 60 to 80% when B20 is used.

Based on emission factors collected from published experimental studies, two emission scenarios were designed aiming to assess biodiesel blends use influence on vehicle exhaust gases emissions and further in air quality over mainland Portugal and the Porto urban area. The reference scenario (REF) considered that biodiesel is not used as fuel by road transport sector and the B20 scenario (B20) assumed that all diesel engines are fuelled with diesel blended with 20% of biodiesel. The emissions for both scenarios were estimated through the emission model TREM-HAP, regarding CO, CO_2, NOx, PM10, PM2.5, total NMVOC, formaldehyde, acetaldehyde, acrolein, and benzene.

In general, the comparison between emission scenarios showed that the introduction of 20% (v/v) of biodiesel in petroleum-based diesel promotes a reduction by 15-20% in CO and by 10% in PM10 and PM2.5 emissions in both case studies. Nevertheless, NOx and carbonyl compounds emissions (acrolein, formaldehyde and acetaldehyde) increased by 5% and more than 20%, respectively. Increments of these carbonyl pollutants, which occur mainly in urban areas, are especially critical due to their reactivity and carcinogenic characteristics, enhancing tropospheric ozone formation and the probability of cancer diseases. On the other hand, experimental studies suggest that dominant VOC of pure diesel engine exhausts (e.g. toluene), with higher chronic hazard quotients and hazard indices than VOC from B20, can sharply decrease when blend fuels are used, which points out to a less injurious characteristics of biodiesel blends against pure fossil diesel to atmospheric pollution and human health. Nevertheless, due to the rise on NOx and carbonyl compounds emissions, a significant increase of the equivalent ozone potential over the most populated regions (the West coast of mainland Portugal, including Lisbon and Porto metropolitan areas) is projected, potentiating the occurrence of photochemical smog.

As expected, the methodology based on road network, applied over the Porto urban area, revealed an improvement in terms of spatial resolution of emissions when compared to mainland Portugal case study. In fact, the emission estimation based on fuel consumption at municipal scale implies a loss of information regarding emission spatial distribution, due to the accounting of line emissions as area sources. The use of road network information to estimate road transport pollutant emission allowed the identification of hotspots located at northeast of the Porto city, which are the major contributors to total pollutant emissions over the Porto urban area.

The REF and B20 emission scenarios were used as input to investigate the effects of biodiesel use on air quality in both case studies. Mainland Portugal was simulated through a domain with 5×5 km^2 of horizontal resolution (PT05) while in the Porto urban area the considered simulation domain had five times finer resolution (OP01). The selection of the WRF-EURAD mesoscale modelling system was carried out based on a multi-model comparison exercise, where EURAD exhibited the best performance at simulating air quality over PT05. However, as indicated by previous works on air quality modelling evaluation, they have important systematic errors (bias) that can be removed by bias-correction techniques. Thus, the WRF-EURAD simulation results were corrected through the application of the RAT04 bias-correction technique, to improve the modelling system performance. In general, the evaluation exercise indicated that the WRF-EURAD-RAT04 system provides suitable air quality simulations within the quality parameters defined for both regional and urban simulation domains. This was the first assessment of WRF-EURAD mesoscale modelling system performance applied at urban scale over Portugal.

Towards achieving clear outcomes on the impact of the B20 fuel use on air quality, both scenario simulations were driven by meteorology regarding the year of 2012 and the same emission data for all the activity sectors with exception of the road transport sector, for which emissions differ according to REF and B20 scenarios. In general, simulation results revealed that B20 scenario promotes reductions up to 25% and 10% for CO and NO_2 concentrations, respectively, on air quality over mainland Portugal, despite the slight increase on NOx emissions for B20 when compared to REF scenario.

Regarding O_3, slight increases on winter-mean concentrations were estimated over the West coast of the territory including urban areas. Nevertheless, pollutants such as PM10, PM2.5 and NMVOC, which have the main emission source not related with road traffic activity, do not assume significant variations over urban areas either in PT05 and OP01.

Differences between scenarios concerning annual-, summer- and winter-mean concentrations of the studied pollutants are negligible over the Porto urban area, with exception to CO, which annual-mean concentrations were reduced in about 5%. Contrary to PT05 domain, NO_2 concentrations slightly increase over OP01. The different approaches used on emissions calculations may be the most obvious reason to explain these contradictory results. On the other hand, OP01 domain may be too small (26×26 km^2) to include all the dynamic and chemical processes of the atmosphere that have an influence over the area of interest. This study also revealed a higher reduction on PM concentrations over the OP01 compared to PT05, which is also justified with the methodology used for emission estimation.

This study suggests that there is a co-benefit from the introduction of biodiesel as a renewable energy and to improve air quality. However, the Portuguese biodiesel supply chain (from the feedstock production to the biodiesel end-use) should be analysed holistically and compared to the reduction on fossil fuels production and consumption in terms of GHG emissions to verify if this chain is truly contributing to the climate change policy and its targets.

The use of a chemical transport model has proved to be crucial to investigate the impacts of atmospheric pollutant emissions on air quality levels, since they react and are converted to other compounds in the atmosphere through complex and non-linear physics and chemical mechanisms. However, future developments should consider non-regulated pollutants emissions (aromatic, PAH and carbonyl compounds), to improve the knowledge on biodiesel blends for road transports impacts on air quality at regional and urban areas, especially in what concerns to tropospheric ozone formation. This type of pollutants should also be considered as individual emission inputs in chemical transport models that should be enhanced to include a more detailed chemical reaction mechanism. Human exposure to aromatic, PAH and carbonyl compounds should also be included in future scientific studies.

Finally, this work represents an important attempt to assess the of EU's and Portuguese efforts related to climate change and energy issues on air quality at regional and urban scales. It allowed to conclude that the use of B20 – the blend fuel that provides higher combustion efficiency and lower exhaust gases emissions – on road transport sector can improve air quality over mainland Portugal, especially in the West coast, and over the Porto urban area.

References

Abd-Alla, G.H., Soliman, H.A., Badr, O.A., Abd-Rabbo, M.F., 2001. Effects of diluent admissions and intake air temperature in exhaust gas recirculation on the emissions of an indirect injection dual fuel engine. Energy Convers. Manag. 42, 1033–1045. doi:10.1016/S0196-8904(00)00072-8

ACAP, 2010. Estatísticas do Sector Automóvel. Lisboa, Portugal.

Ackermann, I.J., Hass, H., Memmesheimer, M., Ebel, A., Binkowski, F.S., Shankar, U., 1998. Modal aerosol dynamics model for Europe. Atmos. Environ. 32, 2981–2999. doi:10.1016/S1352-2310(98)00006-5

AEBIOM - European Biomass Association, 2013. European Bioenergy Outlook 2013. Brussels.

Alves, C., Vicente, A., Nunes, T., Gonçalves, C., Fernandes, A.P., Mirante, F., Tarelho, L., Sánchez de la Campa, A.M., Querol, X., Caseiro, A., Monteiro, C., Evtyugina, M., Pio, C., 2011. Summer 2009 wildfires in Portugal: Emission of trace gases and aerosol composition. Atmos. Environ. 45, 641–649. doi:10.1016/j.atmosenv.2010.10.031

André, J.M., Joumard, R., 2005. Modelling of cold start excess emission for passenger cars.

André, M., 2004. The ARTEMIS European driving cycles for measuring car pollutant emissions. Sci. Total Environ. doi:10.1016/j.scitotenv.2004.04.070

APA, 2014. Portuguese National Inventory Report on greenhouse gases, 1990-2012. Amadora, Portugal.

APA - Agência Portuguesa do Ambiente, 2011. Emissões de Poluentes Atmosféricos por Concelho 2009: Gases acidificantes e eutrofizantes, precursores de ozono, partículas, metais pesados e gases com efeito de estufa. Amadora, Portugal.

APA – Agência Portuguesa do Ambiente, 2012. Roteiro Nacional do Baixo Carbono 2050. Amadora, Portugal.

Aquilina, N., Dudek, A.V., Carvalho, A., Borrego, C., Nordeng, T.E., 2005. MM5 high resolution simulations over Lisbon, in: Geophysical Research Abstracts, Vol. 7, 08685. p. 2. doi:1607-7962/gra/EGU05-A-08685

Arakawa, A., Lamb, V.R., 1977. Computational design for the basic dynamical processes of UCLA general circulation model. Meth. Comp. Phys., 17, 174–264.

Armas, O., Yehliu, K., Boehman, A.L., 2010. Effect of alternative fuels on exhaust emissions during diesel engine operation with matched combustion phasing. Fuel. doi:10.1016/j.fuel.2009.09.022

Aydin, H., Bayindir, H., 2010a. Performance and emission analysis of cottonseed oil methyl ester in a diesel engine. Renew. Energy. doi:10.1016/j.renene.2009.08.009

Aydin, H., Bayindir, H., 2010b. Performance and emission analysis of cottonseed oil methyl ester in a diesel engine. Renew. Energy. doi:10.1016/j.renene.2009.08.009

Bakeas, E., Karavalakis, G., Stournas, S., 2011. Biodiesel emissions profile in modern diesel vehicles. Part 1: Effect of biodiesel origin on the criteria emissions. Sci. Total Environ. 409, 1670–1676. doi:http://dx.doi.org/10.1016/j.scitotenv.2011.01.024

Bakeas, E.B., Argyris, D.I., Siskos, P.A., 2003. Carbonyl compounds in the urban environment of Athens, Greece. Chemosphere 52, 805–813.

Ballesteros, R., Hernández, J.J., Guillén-Flores, J., 2012. Carbonyls speciation in a typical European automotive diesel engine using bioethanol/butanol–diesel blends. Fuel 95, 136–145. doi:10.1016/j.fuel.2011.09.012

Banapurmath, N.R., Tewari, P.G., 2008. Performance of a low heat rejection engine fuelled with low volatile Honge oil and its methyl ester (HOME). Proc. Inst. Mech. Eng. Part A J. Power Energy. doi:10.1243/09576509JPE514

Bergmann, M., Kirchner, U., Vogt, R., Benter, T., 2009. On-road and laboratory investigation of low-level PM emissions of a modern diesel particulate filter equipped diesel passenger car. Atmos. Environ. 43, 1908–1916. doi:http://dx.doi.org/10.1016/j.atmosenv.2008.12.039

Bermúdez, V., Lujan, J.M., Pla, B., Linares, W.G., 2011. Comparative study of regulated and unregulated gaseous emissions during NEDC in a light-duty diesel engine fuelled with Fischer Tropsch and biodiesel fuels. Biomass and Bioenergy 35, 789–798. doi:http://dx.doi.org/10.1016/j.biombioe.2010.10.034

Bessagnet, B., Hodzic, A., Vautard, R., Beekmann, M., Cheinet, S., Honoré, C., Liousse, C., Rouil, L., 2004. Aerosol modeling with CHIMERE—preliminary evaluation at the continental scale. Atmos. Environ. 38, 2803–2817. doi:10.1016/j.atmosenv.2004.02.034

BIOFRAC - BIOFuel Research Advisory Council, 2006. Biofuels in the European Union - a vision for 2030 and beyond. Brussels, Belgium.

Borrego, C., Tchepel, O., Barros, N., Miranda, A.., 2000. Impact of road traffic emissions on air quality of the Lisbon region. Atmos. Environ. doi:10.1016/S1352-2310(00)00301-0

Borrego, C., Tchepel, O., Costa, A.M., Amorim, J.H., Miranda, A.I., 2003. Emission and dispersion modelling of Lisbon air quality at local scale, in: Atmospheric Environment. pp. 5197–5205. doi:10.1016/j.atmosenv.2003.09.004

Borrego, C., Tchepel, O., Salmim, L., Amorim, J.H., Costa, A.M., Janko, J., 2004. Integrated Modeling of Road Traffic Emissions: Application to Lisbon Air Quality Management. Cybern. Syst. 35, 14p. doi:10.1080/0196972049051904

Borrego, C., Monteiro, A., Ferreira, J., Miranda, A.I., Costa, A.M., Carvalho, A.C., Lopes, M., 2008. Procedures for estimation of modelling uncertainty in air quality assessment. Environ. Int. 34, 613–20. doi:10.1016/j.envint.2007.12.005

Borrego, C., Miranda, A.I., Ferreira, J., Tchepel, O., Monteiro, A., Dias, D., Ribeiro, I., Tavares, R., Barbedo, P., 2009. Melhoria do actual inventário de emisões de poluentes atmosféricos da Região Norte (AMB – QA – 09/2009). Aveiro, Portugal.

Borrego, C., Monteiro, A., Pay, M.., Ribeiro, I., Miranda, A.., Basart, S., Baldasano, J.., 2011. How bias-correction can improve air quality forecasts over Portugal. Atmos. Environ. doi:10.1016/j.atmosenv.2011.09.006

Bott, A., 1989. A Positive Definite Advection Scheme Obtained by Nonlinear Renormalization of the Advective Fluxes. Mon. Weather Rev. 117, 1006–1016. doi:http://dx.doi.org/10.1175/1520-0493(1989)117<1006:APDASO>2.0.CO;2

Boulter, P.G., McCrae, I.S., 2007. ARTEMIS : Assessment and Reliability of Transport Emission Models and Inventory Systems – final report, 2007.

Bringezu, S., Schütz, H., O'Brien, M., Kauppi, L., Howarth, R.W., McNeely, J., 2009. Towards sustainable production and use of resources: Assessing Biofuels. United Nations Environmental Programme, Paris, France.

Canakci, M., Gerpen, J.H. Van, 2001. Comparison of Engine Performance and Emissions for Petroleum Diesel Fuel , Yellow Grease Biodiesel , and Soybean Oil Biodiesel. Trans. Am. Soc. Agric. Eng. 46, 937–944.

Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manag. Assoc. 44, 881–899.

Carter, W.P.L., 2009. Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications. Prep. Californian air Resour. board Contract 07-339; 2010.

Carvalho, A., Monteiro, A., Ribeiro, I., Tchepel, O., Miranda, A.I., Borrego, C., Saavedra, S., Souto, J.A., Casares, J.J., 2010a. High ozone levels in the northeast of Portugal: Analysis and characterization. Atmos. Environ. doi:10.1016/j.atmosenv.2009.12.020

Carvalho, A.C., Carvalho, A., Gelpi, I., Barreiro, M., Borrego, C., Miranda, A.I., Pérez-Muñuzuri, V., 2006. Influence of topography and land use on pollutants dispersion in the Atlantic coast of Iberian Peninsula. Atmos. Environ. 40, 3969–3982. doi:10.1016/j.atmosenv.2006.02.014

Carvalho, T.B., Brito, P.S.D., Oliveira, A.., 2010b. Gaseificação térmica de resíduos sólidos da indústria do azeite, in: 1st International Congress on Bioenergy. Portalegre, Portugal, p. 6.

Chang, C.-C., Lo, J.-G., Wang, J.-L., 2001. Assessment of reducing ozone forming potential for vehicles using liquefied petroleum gas as an alternative fuel. Atmos. Environ. 35, 6201–6211. doi:10.1016/S1352-2310(01)00386-7

Chauhan, B.S., Kumar, N., Cho, H.M., 2012. A study on the performance and emission of a diesel engine fueled with Jatropha biodiesel oil and its blends. Energy 37, 616–622. doi:10.1016/j.energy.2011.10.043

Chen, H., Shi-Jin, S., Jian-Xin, W., 2007. Study on combustion characteristics and PM emission of diesel engines using ester–ethanol–diesel blended fuels. Proc. Combust. Inst. doi:10.1016/j.proci.2006.07.130

Cheung, C.S., Zhu, L., Huang, Z., 2009. Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. Atmos. Environ. 43, 4865–4872. doi:10.1016/j.atmosenv.2009.07.021

Corrêa, S., Arbilla, G., 2008. Carbonyl emissions in diesel and biodiesel exhaust. Atmos. Environ. 42, 769–775. doi:10.1016/j.atmosenv.2007.09.073

COST Action 732, 2009. Model evaluation case studies: aproach and results - Quality assurance and improvement of microscale meteorological models. Brussels, Belgium.

De Alegría Mancisidor, I.M., Díaz de Basurto Uraga, P., Martínez de Alegría Mancisidor, I., Ruiz de Arbulo López, P., 2009. European Union's renewable energy sources and energy efficiency policy review: The Spanish perspective. Renew. Sustain. Energy Rev. 13, 100–114. doi:10.1016/j.rser.2007.07.003

Delle Monache, L., Nipen, T., Deng, X., Zhou, Y., Stull, R., 2006. Ozone ensemble forecasts: 2. A Kalman filter predictor bias correction. J. Geophys. Res. doi:10.1029/2005JD006311

Delle Monache, L., Wilczark, J., McKeen, S., Grell, G., Pagowski, M., Peckham, S., Stull, R., McHenry, J., McQueen, J., 2008. A Kalman-filter bias correction method applied to deterministic, ensemble averaged and probabilistic forecasts of surface ozone. Tellus B 60, 238–249. doi:10.1111/j.1600-0889.2007.00332.x

Demirbas, A., 2007. Importance of biodiesel as transportation fuel. Energy Policy 35, 4661–4670. doi:10.1016/j.enpol.2007.04.003

Demirbas, A., 2009. Biofuels – Securing the Planet's Future Energy Needs. Springer, Heidelberg, Germany. doi:10.1007/978-1-84882-011-1

Demirbas, A., 2009. Progress and recent trends in biodiesel fuels. Energy Convers. Manag. 50, 14–34. doi:10.1016/j.enconman.2008.09.001

Denby, B., Horálek, J., Walker, S.E., Eben, K., 2005. Interpolation and assimilation methods for European scale air quality assessment and mapping - Part I: Review and recommendations ETC/ACC Technical Paper 2005/7.

Denby, B., Spangl, W., 2010. The combined use of models and monitoring for applications related to the european air quality directive : a working sub-group of FAIRMODE, in: 13th Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes. p. 6.

Dennis, R., Fox, T., Fuentes, M., Gilliland, A., Hanna, S., Hogrefe, C., Irwin, J., Rao, S.T., Scheffe, R., Schere, K., Steyn, D., Venkatram, A., 2010. A framework for evaluating regional-scale numerical photochemical modeling systems. Environ. Fluid Mech. 10, 471–489. doi:10.1007/s10652-009-9163-2

DGEG - Direcção Geral de Energia e Geologia, 2013. Portugal - Key energy statistics. Lisboa, Portugal.

Di, Y., Cheung, C.S., Huang, Z., 2009. Experimental investigation on regulated and unregulated emissions of a diesel engine fueled with ultra-low sulfur diesel fuel blended with biodiesel from waste cooking oil. Sci. Total Environ. 407, 835–846. doi:10.1016/j.scitotenv.2008.09.023

Dias, J.M., Costa, J.F., Alvim-Ferraz, M.C.M., Almeida, M, F., 2012. Biodiesel production from olive oil bagasse, in: 1st International Congress on Bioenergy. Portalegre, Portugal, p. 6.

Dings, J., 2013. Mind the gap! Why official car fuel economy figures don’t match up to reality.

Djalalova, I., Wilczak, J., McKeen, S., Grell, G., Peckham, S., Pagowski, M., DelleMonache, L., McQueen, J., Tang, Y., Lee, P., 2010. Ensemble and bias-correction techniques for air quality model forecasts of surface O3 and PM2.5 during the TEXAQS-II experiment of 2006. Atmos. Environ. doi:10.1016/j.atmosenv.2009.11.007

Ebel, A., Elbern, H., Feldmann, H., Jakobs, H.J., Kessler, C., Memmesheimer, M., Oberreuter, A., Piekorz, G., 1997. Air pollution studies with the EURAD model system (3).

EEA, 2012. Greenhouse gas emission trends and projections in Europe 2012, Europe. Copenhagen, Denmark. doi:10.2800/56770

EEA, 2013. A closer look at urban transport. TERM 2013: transport indicators tracking progress towards environmental targets in Europe. Copenhagen, Denmark.

Elbern, H., Strunk, A., Schmidt, H., Talagrand, O., 2007. Emission rate and chemical state estimation by 4-dimensional variational inversion. Atmos. Chem. Phys. 7, 3749–3769. doi:10.5194/acp-7-3749-2007

Elbern, H., Friese, E., 2013. MACC II deliverables: EURAD-IM regional forecasting system and performances.

Elbir, T., 2003. Comparison of model predictions with the data of an urban air quality monitoring network in Izmir, Turkey. Atmos. Environ. 37, 2149–2157. doi:10.1016/S1352-2310(03)00087-6

EMEP, 2013. Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe. PART I. Unified EMEP Model Description. EMEP Report 1/2003.

EMEP/EEA, 2013. EMEP/EEA air pollutant emission inventory guidebook 2013.

EPA, 2002. A comprehensive analysis of biodiesel impacts on exhaust emissions. United States.

EurObserv’ER, 2013. Biofuels Baramoter. Paris, France.

EUROSTAT, 2013. Energy consumption EU27 energy dependence rate at 54% in 2011 Energy consumption down by 6% between 2008 and 2011. (ref. STAT/13/23).

EUROSTAT, 2014. Renewable energy in the EU28 - 37/2014, EUROSTAT news release.

Evtyugina, M., Calvo, A.I., Nunes, T., Alves, C., Fernandes, A.P., Tarelho, L., Vicente, A., Pio, C., 2013. VOC emissions of smouldering combustion from Mediterranean wildfires in central Portugal. Atmos. Environ. doi:10.1016/j.atmosenv.2012.10.001

Felipe, Á., Ortuño, M.T., Righini, G., Tirado, G., 2014. A heuristic approach for the green vehicle routing problem with multiple technologies and partial recharges. Transp. Res. Part E Logist. Transp. Rev. 71, 111–128. doi:10.1016/j.tre.2014.09.003

Fernandes, S., Gaspar, A., 2012. Valorização da biomassa florestal: pre-extrações e hidrólise de polissacarídeos a açúcares simples para a bioindústria (ex. bioethanol), in: 1st International Congress on Bioenergy. Portalegre, Portugal, p. 6.

Fernández, J., Montávez, J.P., Sáenz, J., González-Rouco, J.F., Zorita, E., 2007. Sensitivity of the MM5 mesoscale model to physical parameterizations for regional climate studies: Annual cycle. J. Geophys. Res. Atmos. 112. doi:10.1029/2005JD006649

Fischer, G., Prr, S., van Velthuizen, H., Lensink, S.M., Londo, M., de Wit, M., 2010. Biofuel production potentials in Europe: Sustainable use of cultivated land and pastures. Part I: Land productivity potentials. Biomass and Bioenergy 34, 159–172. doi:http://dx.doi.org/10.1016/j.biombioe.2009.07.008

Fontaras, G., Karavalakis, G., Kousoulidou, M., Tzamkiozis, T., Ntziachristos, L., Bakeas, E., Stournas, S., Samaras, Z., 2009. Effects of biodiesel on passenger car fuel consumption, regulated and non-regulated pollutant emissions over legislated and real-world driving cycles. Fuel 88, 1608–1617. doi:10.1016/j.fuel.2009.02.011

Fontaras, G., Kousoulidou, M., Karavalakis, G., Tzamkiozis, T., Pistikopoulos, P., Ntziachristos, L., Bakeas, E., Stournas, S., Samaras, Z., 2010. Effects of low concentration biodiesel blend application on modern passenger cars. Part 1: Feedstock impact on regulated pollutants, fuel consumption and particle emissions. Environ. Pollut. 158, 1451–1460. doi:http://dx.doi.org/10.1016/j.envpol.2009.12.033

Fontaras, G., Franco, V., Dilara, P., Martini, G., Manfredi, U., 2014. Development and review of Euro 5 passenger car emission factors based on experimental results over various driving cycles. Sci. Total Environ. 468-469, 1034–42. doi:10.1016/j.scitotenv.2013.09.043

Gaffney, J.S., Marley, N.A., 2009. The impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond. Atmos. Environ. 43, 23–36. doi:http://dx.doi.org/10.1016/j.atmosenv.2008.09.016

Galmarini, S., Bianconi, R., Klug, W., Mikkelsen, T., Addis, R., Andronopoulos, S., Astrup, P., Baklanov, A., Bartniki, J., Bartzis, J.C., Bellasio, R., Bompay, F., Buckley, R., Bouzom, M., Champion, H., D'Amours, R., Davakis, E., Eleveld, H., Geertsema, G.T., Glaab, H., Kollax, M., Ilvonen, M., Manning, A., Pechinger, U., Persson, C., Polreich, E., Potemski, S., Prodanova, M., Saltbones, J., Slaper, H., Sofiev, M.A., Syrakov, D., Sørensen, J.H., Auwera, L.V. der, Valkama, I., Zelazny, R., 2004. Ensemble dispersion forecasting—Part I: concept, approach and indicators. Atmos. Environ. doi:10.1016/j.atmosenv.2004.05.030

Galp, 2012a. Refinaria de Matosinhos – Data book de segurança. Saúde e Ambiente 2011.

Galp, 2012b. Refinaria de Sines – Data book de segurança. Saúde e Ambiente 2011.

Garber, W., Colosio, J., Grittner, S., Larssen, S., Rasse, D., Schneider, J., Houssiau, M., 2002. Guidance on the Annexes to Decision 97/101/EC on Exchange of Information as Revised by Decision 2001/752/EC.

Geiger, H., Barnes, I., Bejan, I., Benter, T., Spittler, M., 2003. The tropospheric degradation of isoprene: an updated module for the regional atmospheric chemistry mechanism. Atmos. Environ. 37, 1503–1519. doi:10.1016/S1352-2310(02)01047-6

Ghobadian, B., Rahimi, H., Nikbakht, A.M., Najafi, G., Yusaf, T.F., 2009. Diesel engine performance and exhaust emission analysis using waste cooking biodiesel fuel with an artificial neural network. Renew. Energy 34, 976–982. doi:10.1016/j.renene.2008.08.008

Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. J. Geophys. Res. doi:10.1029/93JD00527

Gumus, M., 2008. Evaluation of hazelnut kernel oil of Turkish origin as alternative fuel in diesel engines. Renew. Energy 33, 2448–2457. doi:10.1016/j.renene.2008.02.005

Gumus, M., Kasifoglu, S., 2010. Performance and emission evaluation of a compression ignition engine using a biodiesel (apricot seed kernel oil methyl ester) and its blends with diesel fuel. Biomass and Bioenergy 34, 134–139. doi:10.1016/j.biombioe.2009.10.010

Gupta, R.B., Demirbas, A., 2010. Gasoline, diesel and etanol biofuels from grasses and plants, 1st ed. Cambridge University Press, New York.

Hanna, S.R., Chang, J.C., Strimaitis, D.G., 1993. Hazardous gas model evaluation with field observations. Atmos. Environ. Part A. Gen. Top. 27, 2265–2285. doi:10.1016/0960-1686(93)90397-H

Hass, H., 1991. Description of the EURAD Chemistry-Transport-Model version2 (CTM2). Cologne.

He, C., Ge, Y., Tan, J., You, K., Han, X., Wang, J., 2010. Characteristics of polycyclic aromatic hydrocarbons emissions of diesel engine fueled with biodiesel and diesel. Fuel 89, 2040–2046. doi:10.1016/j.fuel.2010.03.014

He, Y., Wang, S., Lai, K.K., 2010. Global economic activity and crude oil prices: A cointegration analysis. Energy Econ. 32, 868–876. doi:http://dx.doi.org/10.1016/j.eneco.2009.12.005

Heywood, J.B., 1988. Internal Combustion Engine Fundamentals, McGrawHill series in mechanical engineering.

Ho, K.F., Sai Hang Ho, S., Cheng, Y., Lee, S.C., Zhen Yu, J., 2007. Real-world emission factors of fifteen carbonyl compounds measured in a Hong Kong tunnel. Atmos. Environ. 41, 1747–1758. doi:10.1016/j.atmosenv.2006.10.027

Holtslag, A.A.M., Nieuwstadt, F.T.M., 1986. Scaling the atmospheric boundary layer. Boundary-Layer Meteorol. 36, 201–209. doi:10.1007/BF00117468

Hong, S.-Y., Lim, H.-O.J., 2006. The WRF single-moment 6-class microphysics scheme (WSM6). J. Korean Meteorol. Soc. 42, 129–151.

Hurley, P., Manins, P., Lee, S., Boyle, R., Ng, Y.L., Dewundege, P., 2003. Year-long, high-resolution, urban airshed modelling: verification of TAPM predictions of smog and particles in Melbourne, Australia. Atmos. Environ. doi:10.1016/S1352-2310(03)00047-5

IEA, 2013. Key world energy statistics 2013. International Energy Agency, OECD/IEA, Paris.

IPCC, 2007. Climate Change 2007 : An Assessment of the Intergovernmental Panel on Climate Change, Change. Cambridge University Press. doi:10.1256/004316502320517344

Jacobson, M.Z., 2007. Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States. Environ. Sci. Technol. 41, 4150–4157. doi:10.1021/es062085v

Janjić, Z.I., 1994. The Step-Mountain Eta Coordinate Model: Further Developments of the Convection, Viscous Sublayer, and Turbulence Closure Schemes. Mon. Weather Rev. doi:10.1175/1520-0493(1994)122<0927:TSMECM>2.0.CO;2

Jonson, J.E., Tarrasón, L., Klein, H., Vestreng, V., Cofala, J., Whall, C., 2009. Effects of ship emissions on European ground-level ozone in 2020. Int. J. Remote Sens. 30, 4099–4110. doi:10.1080/01431160902821858

Kain, J.S., 2004. The Kain–Fritsch Convective Parameterization: An Update. J. Appl. Meteorol. doi:10.1175/1520-0450(2004)043<0170:TKCPAU>2.0.CO;2

Kalligeros, S., Zannikos, F., Stournas, S., Lois, E., Anastopoulos, G., Teas, C., Sakellaropoulos, F., 2003. An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine. Biomass and Bioenergy 24, 141–149. doi:10.1016/S0961-9534(02)00092-2

Kang, D., Eder, B.K., Stein, A.F., Grell, G.A., Peckham, S.E., McHenry, J., 2005. The New England Air Quality Forecasting Pilot Program: development of an evaluation protocol and performance benchmark. J. Air Waste Manag. Assoc. 55, 1782–1796. doi:10.1080/10473289.2005.10464775

Kang, D., Mathur, R., Rao, S.T., Yu, S., 2008. Bias adjustment techniques for improving ozone air quality forecasts. J. Geophys. Res. Atmos. 113, n/a–n/a. doi:10.1029/2008JD010151

Karavalakis, G., Stournas, S., Bakeas, E., 2009. Effects of diesel/biodiesel blends on regulated and unregulated pollutants from a passenger vehicle operated over the European and the Athens driving cycles. Atmos. Environ. 43, 1745–1752. doi:http://dx.doi.org/10.1016/j.atmosenv.2008.12.033

Karavalakis, G., Deves, G., Fontaras, G., Stournas, S., Samaras, Z., Bakeas, E., 2010. The impact of soy-based biodiesel on PAH, nitro-PAH and oxy-PAH emissions from a passenger car operated over regulated and nonregulated driving cycles. Fuel 89, 3876–3883. doi:10.1016/j.fuel.2010.07.002

Karavalakis, G., Bakeas, E., Fontaras, G., Stournas, S., 2011a. Effect of biodiesel origin on regulated and particle-bound PAH (polycyclic aromatic hydrocarbon) emissions from a Euro 4 passenger car. Energy 36, 5328–5337. doi:http://dx.doi.org/10.1016/j.energy.2011.06.041

Karavalakis, G., Boutsika, V., Stournas, S., Bakeas, E., 2011b. Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions. Sci. Total Environ. 409, 738–47. doi:10.1016/j.scitotenv.2010.11.010

Kidoguchi, Y., 2000. Effects of fuel cetane number and aromatics on combustion process and emissions of a direct-injection diesel engine. JSAE Rev. doi:10.1016/S0389-4304(00)00075-8

Knothe, G., Sharp, C.A., Ryan, T.W., 2006. Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and Alkanes in a New Technology Engine. Energy & Fuels 20, 403–408. doi:10.1021/ef0502711

Knothe, G., 2014. A comprehensive evaluation of the cetane numbers of fatty acid methyl esters. Fuel 119, 6–13.

Korres, D.M., Karonis, D., Lois, E., Linck, M.B., Gupta, A.K., 2008. Aviation fuel JP-5 and biodiesel on a diesel engine. Fuel. doi:10.1016/j.fuel.2007.04.004

Kousoulidou, M., Ntziachristos, L., Fontaras, G., Martini, G., Dilara, P., Samaras, Z., 2012. Impact of biodiesel application at various blending ratios on passenger cars of different fueling technologies. Fuel 98, 88–94. doi:http://dx.doi.org/10.1016/j.fuel.2012.03.038

Krahl, J., Baum, K., Hackbarth, U., Jeberien, H. –E., Munack, A., Schütt, C., Schröder, O., Walter, N., Bünger, J., Müller, M.M., Weigel, A., 2001. Gaseous compounds, ozone precursors, particle number and particle size distributions, and mutagenic effects due to biodiesel. Am. Soc. Agric. Biol. Eng. 44, 179–191. doi:doi: 10.13031/2013.4675

Krahl, J., Munack, A., Schroder, O., Dutz, M., Bunger, J., 2002. Exhaust Gas Emissions and Health Effects from Biodiesel, Fossil Diesel Fuel, and Swedish Low Sulfur Diesel Fuel MKI. ASEA 02-6082. doi:10.13031/2013.9771

Krahl, J., Munack, A., Schröder, O., Stein, H., Al., E., 2003. Influence of Biodiesel and Different Designed Diesel Fuels on the Exhaust Gas Emissions and Health Effects. SAE. doi:doi:10.4271/2003-01-3199

Krasuska, E., Cadorniga, C., Tenorio, J.L., Testa, G., Scordia, D., 2010. Potential land availability for energy crops production in Europe. Biofuels Bioprod. Biorefining-Biofpr 4, 658–673. doi:10.1002/bbb.259

Kumar, M.S., Ramesh, A., Nagalingam, B., 2009. A Comparison of the Different Methods of Using Jatropha Oil as Fuel in a Compression Ignition Engine. J. Eng. Gas Turbines Power 132, 32801.

Kumar, N., Chauhan, S.R., 2013. Performance and emission characteristics of biodiesel from different origins: A review. Renew. Sustain. Energy Rev. 21, 633–658. doi:10.1016/j.rser.2013.01.006

Kumar, S., Singh, J., Nanoti, S.M., Garg, M.O., 2012. A comprehensive life cycle assessment (LCA) of Jatropha biodiesel production in India. Bioresour. Technol. 110, 723–729. doi:10.1016/j.biortech.2012.01.142

Kwanchareon, P., Luengnaruemitchai, A., Jai-In, S., 2007. Solubility of a diesel–biodiesel–ethanol blend, its fuel properties, and its emission characteristics from diesel engine. Fuel. doi:10.1016/j.fuel.2006.09.034

Lapuerta, M., Armas, O., Rodríguez-Fernández, J., 2008. Effect of biodiesel fuels on diesel engine emissions. Prog. Energy Combust. Sci. 34, 198–223. doi:http://dx.doi.org/10.1016/j.pecs.2007.07.001

Lavoie, G., Heywood, J., Keck, J., 1970. Experimental and Theoretical Study of Nitric Oxide Formation in Internal Combustion Engines. Combust. Sci. Technol. 1, 313–326. doi:10.1080/00102206908952211

Lin, B.-F., Huang, J.-H., Huang, D.-Y., 2009. Experimental study of the effects of vegetable oil methyl ester on DI diesel engine performance characteristics and pollutant emissions. Fuel. doi:10.1016/j.fuel.2009.04.006

Lin, C.Y., Lin, H.A., 2007. Engine performance and emission characteristics of a three-phase emulsion of biodiesel produced by peroxidation. Fuel Process. Technol. 88, 35–41. doi:10.1016/j.fuproc.2006.07.008

Lin, C.-Y., Fan, C.-L., 2011. Fuel properties of biodiesel produced from Camellia oleifera Abel oil through supercritical-methanol transesterification. Fuel 90, 2240–2244. doi:10.1016/j.fuel.2011.02.020

Liu, Y.-Y., Lin, T.-C., Wang, Y.-J., Ho, W.-L., 2009. Carbonyl Compounds and Toxicity Assessments of Emissions from a Diesel Engine Running on Biodiesels. J. Air Waste Manage. Assoc. 59, 163–171. doi:10.3155/1047-3289.59.2.163

Lopes, M., Serrano, L., Ribeiro, I., Cascão, P., Pires, N., Rafael, S., Tarelho, L., Monteiro, A., Nunes, T., Evtyugina, M., Nielsen, O.J., Gameiro da Silva, M., Miranda, A.I., Borrego, C., 2014. Emissions characterization from EURO 5 diesel/biodiesel passenger car operating under the new European driving cycle. Atmos. Environ. 84, 339–348. doi:http://dx.doi.org/10.1016/j.atmosenv.2013.11.071

Lupiáñez, C., Guedea, I., Bolea, I., Díez, L.I., Romeo, L.M., 2013. Experimental study of SO2 and NOx emissions in fluidized bed oxy-fuel combustion. Fuel Process. Technol. 106, 587–594. doi:http://dx.doi.org/10.1016/j.fuproc.2012.09.030

Macor, A., Avella, F., Faedo, D., 2011. Effects of 30 % v / v biodiesel / diesel fuel blend on regulated and unregulated pollutant emissions from diesel engines. Appl. Energy 88, 4989–5001. doi:10.1016/j.apenergy.2011.06.045

Madronich, S., 1987. Photodissociation in the atmosphere: 1. Actinic flux and the effects of ground reflections and clouds. J. Geophys. Res. doi:10.1029/JD092iD08p09740

Malça, J., Freire, F., 2011. Life-cycle studies of biodiesel in Europe: A review addressing the variability of results and modeling issues. Renew. Sustain. Energy Rev. doi:10.1016/j.rser.2010.09.013

Mani, M., Subash, C., Nagarajan, G., 2009. Performance, emission and combustion characteristics of a DI diesel engine using waste plastic oil. Appl. Therm. Eng. 29, 2738–2744. doi:10.1016/j.applthermaleng.2009.01.007

McCormick, R.L., Williams, A., Ireland, J., Brimhall, M., Hayes, R.R., 2006. Effects of Biodiesel Blends on Vehicle Emissions (Milestone Report NREL/MP-540-40554 October 2006). Colorado, USA.

McKeen, S., Wilczak, J., Grell, G., Djalalova, I., Peckham, S., Hsie, E.-Y., Gong, W., Bouchet, V., Menard, S., Moffet, R., McHenry, J., McQueen, J., Tang, Y., Carmichael, G.R., Pagowski, M., Chan, A., Dye, T., Frost, G., Lee, P., Mathur, R., 2005. Assessment of an ensemble of seven real-time ozone forecasts over eastern North America during the summer of 2004. J. Geophys. Res. doi:10.1029/2005JD005858

MEID - Ministério da economia inovação e desenvolvimento, 2010. National Energy Strategy 2020 - Decreto-Lei n.º 117/2010. Diário da República, 1.ª série - N.º 207 - 25 de Outubro de 2010, Lisbon, Portugal.

Memmesheimer, M., Tippke, A., Ebel, H., Hass, H.J., Jakobs, M., Laube, 1991. On the use of EMEP emission inventories for European scale air pollution modeling with the EURAD model, in: EMEP Workshop on Photooxidant Modelling for Long-Range Transport in Relation to Abatement Strategies, Berlin, 16.-19. April 1991,. pp. 307–324.

Miranda, A.I., Borrego, C., Monteiro, A., Tchepel, O., Ribeiro, I., Monteiro, A.C., Fernandes, A.P., 2012. Avaliação da qualidade do ar para efeitos de reporting à Comissão Europeia – 2010 e 2011. Protocolo APA/UA 2011-2013, Avaliação e previsão da qualidade do ar em Portugal – R2. Aveiro.

Misenis, C., Zhang, Y., 2010. An examination of sensitivity of WRF/Chem predictions to physical parameterizations, horizontal grid spacing, and nesting options. Atmos. Res. 97, 315–334. doi:10.1016/j.atmosres.2010.04.005

MOBI.E - Mobilidade elétrica, 2013. MOBI.E - Mobilidade elétrica [WWW Document]. URL http://www.mobie.pt/

Monteiro, A., Strunk, A., Carvalho, A., Tchepel, O., Miranda, A.I., Borrego, C., Saavedra, S., Rodríguez, A., Souto, J., Casares, J., Friese, E., Elbern, H., 2012. Investigating a high ozone episode in a rural mountain site. Environ. Pollut. doi:10.1016/j.envpol.2011.11.008

Monteiro, A., Ribeiro, I., Tchepel, O., Sá, E., Ferreira, J., Carvalho, A., Martins, V., Strunk, A., Galmarini, S., Elbern, H., Schaap, M., Builtjes, P., Miranda, A.I., Borrego, C., 2013a. Bias Correction Techniques to Improve Air Quality Ensemble Predictions: Focus on O3 and PM Over Portugal. Environ. Model. Assess. 18, 533–546. doi:10.1007/s10666-013-9358-2

Monteiro, A., Ribeiro, I., Tchepel, O., Carvalho, A., Martins, H., Sá, E., Ferreira, J., Martins, V., Galmarini, S., Miranda, A.I., Borrego, C., 2013b. Ensemble Techniques to Improve Air Quality Assessment: Focus on O3 and PM. Environ. Model. Assess. 18, 249–257. doi:10.1007/s10666-012-9344-0

Monyem, A., Gerpen, J.H. Van, Canakci, M., 2001. The effect of timing and oxidation on emissions from biodiesel-fueled engines. Trans. Am. Soc. Agric. Eng. 44, 35–42.

Nabi, M.N., Rahman, M.M., Akhter, M.S., 2009. Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. Appl. Therm. Eng. 29, 2265–2270. doi:10.1016/j.applthermaleng.2008.11.009

Nanaki, E.A., Koroneos, C.J., 2012. Comparative LCA of the use of biodiesel, diesel and gasoline for transportation. J. Clean. Prod. 20, 14–19. doi:10.1016/j.jclepro.2011.07.026

NCEP/NOAA, 2000. NCEP FNL Operational Model Global Tropospheric Analyses, continuing from July 1999. doi:10.5065/D6M043C6

Nieradzik, L., 2011. Four-Dimensional Variational Assimilation of Aerosol Data from In-situ and Remote Sensing Platforms. University of Cologne.

Nieradzik, L.P., 2005. Application of a High Dimensional Model Representation on the Atmospheric Aerosol Module MADE of the EURAD-CTM. University of Cologne.

Nigam, P.S., Singh, A., 2011. Production of liquid biofuels from renewable resources. Prog. Energy Combust. Sci. doi:10.1016/j.pecs.2010.01.003

Ntziachristos, L., Gkatzoflias, D., Kouridis, C., Samaras, Z., 2009. COPERT: A European Road Transport Emission Inventory Model, in: Athanasiadis, I., Rizzoli, A., Mitkas, P., Gómez, J. (Eds.), Information Technologies in Environmental Engineering SE - 37, Environmental Science and Engineering. Springer Berlin Heidelberg, pp. 491–504. doi:10.1007/978-3-540-88351-7_37

Observ'ER, 2013. The state of renewable energies in Europe.

Olesen, H.R., 2001. Ten years of harmonization activities: past, present and future., in: 7th Int. Conf. on Harmonization within Atmospheric Dispersion Modelling for Regulatory Purposes. Belgirate, Italy, p. 10.

Öner, C., Altun, Ș., 2009. Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine. Appl. Energy. doi:10.1016/j.apenergy.2009.01.005

Peng, C.-Y., Yang, H.-H., Lan, C.-H., Chien, S.-M., 2008. Effects of the biodiesel blend fuel on aldehyde emissions from diesel engine exhaust. Atmos. Environ. 42, 906–915. doi:http://dx.doi.org/10.1016/j.atmosenv.2007.10.016

Peng, C.-Y., Lan, C.-H., Yang, C.-Y., 2012. Effects of biodiesel blend fuel on volatile organic compound (VOC) emissions from diesel engine exhaust. Biomass and Bioenergy. doi:10.1016/j.biombioe.2011.10.016

Pleim, J.E., 2007. A Combined Local and Nonlocal Closure Model for the Atmospheric Boundary Layer. Part II: Application and Evaluation in a Mesoscale Meteorological Model. J. Appl. Meteorol. Climatol. doi:10.1175/JAM2534.1

Poeschl, U., Von Kuhlmann, R., Poisson, N., Crutzen, P.J., 2000. Development and intercomparison of condensed isoprene oxidation mechanisms for global atmospheric modeling. J. Atmos. Chem. 37, 29–52. doi:10.1023/A:1006391009798

Qi, D.H., Chen, H., Geng, L.M., Bian, Y.Z., 2010. Experimental studies on the combustion characteristics and performance of a direct injection engine fueled with biodiesel/diesel blends. Energy Convers. Manag. 51, 2985–2992.

Ramadhas, A.S., Muraleedharan, C., Jayaraj, S., 2005. Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. Renew. Energy. doi:10.1016/j.renene.2005.01.009

Ramadhas, A.S., Jayaraj, S., Muraleedharan, C., Padmakumari, K., 2006. Artificial neural networks used for the prediction of the cetane number of biodiesel. Renew. Energy 31, 2524–2533. doi:10.1016/j.renene.2006.01.009

Randazzo, M.L., Sodré, J.R., 2011. Exhaust emissions from a diesel powered vehicle fuelled by soybean biodiesel blends (B3–B20) with ethanol as an additive (B20E2–B20E5). Fuel 90, 98–103. doi:10.1016/j.fuel.2010.09.010

Regnier, E., 2007. Oil and energy price volatility. Energy Econ. 29, 405–427. doi:10.1016/j.eneco.2005.11.003

Rettenmaier, N., Köppen, S., Gärtner, S.O., Reinhardt, G.A., 2010. Life cycle assessment of selected future energy crops for Europe. Biofuels, Bioprod. Biorefining 4, 620–636. doi:10.1002/bbb.245

Ribeiro, I., 2008. Análise da previsão da qualidade do ar em Portugal Continental durante 2007-2008 (MS.c thesis). University of Aveiro.

Ribeiro, I., Tavares, A.M., Sá, E., Lopes, M., 2011. Impacts of Biofuels on Air Quality: Northern Portugal Case Study, in: International Conference on Climate Change and Global Warming 2011. 28-30 November 2011, Venice, Italy. Vol. 59. World Academy of Science, Engineering and Technology, pp. 12889 – 12894.

Ribeiro, I., Cascão, P., Monteiro, A., Lopes, M., Tavares, R., Figueira de Sousa, J., Miranda, A.I., Borrego, C., 2012. The impact of biodiesel on air pollutant emissions: Northern Portugal case study, in: 32nd Annual Meeting of the International Association for Impact Assessment - Energy Future The Role of Impact Assessment. 27 May- 1 June 2012, Porto, Portugal. p. 6.

Ribeiro, I., Valente, J., Amorim, J., Miranda, A., Lopes, M., Borrego, C., Monteiro, A., 2014. Air Quality Modelling and Its Applications, in: Cao, G., Orrù, R. (Eds.), Current Environmental Issues and Challenges SE - 3. Springer Netherlands, pp. 45–56. doi:10.1007/978-94-017-8777-2_3

Roselle, S., Binkowski, F., 1999. Capter 11: Cloud dynamics and chemistry. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. EPA Report EPA/600/R-99/030., Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. U.S.A.

Rosillo-Calle, F., Cortez, L.A.B., 1998. Towards ProAlcool II—a review of the Brazilian bioethanol programme. Biomass and Bioenergy 14, 115–124. doi:10.1016/S0961-9534(97)10020-4

Rounce, P., Tsolakis, A., York, A.P.E., 2012. Speciation of particulate matter and hydrocarbon emissions from biodiesel combustion and its reduction by aftertreatment. Fuel 96, 90–99. doi:http://dx.doi.org/10.1016/j.fuel.2011.12.071

Sahoo, P.K., Das, L.M., Babu, M.K.G., Arora, P., Singh, V.P., Kumar, N.R., Varyani, T.S., 2009. Comparative evaluation of performance and emission characteristics of jatropha, karanja and polanga based biodiesel as fuel in a tractor engine. Fuel 88, 1698–1707. doi:10.1016/j.fuel.2009.02.015

Sanz Requena, J.F., Guimaraes, A.C., Quirós Alpera, S., Relea Gangas, E., Hernandez-Navarro, S., Navas Gracia, L.M., Martin-Gil, J., Fresneda Cuesta, H., 2011. Life Cycle Assessment (LCA) of the biofuel production process from sunflower oil, rapeseed oil and soybean oil. Fuel Process. Technol. 92, 190–199. doi:10.1016/j.fuproc.2010.03.004

Savaliya, M., Dhorajiya, B., Dholakiya, B., 2013. Recent advancement in production of liquid biofuels from renewable resources: a review. Res. Chem. Intermed. 1–35. doi:10.1007/s11164-013-1231-z

Schaap, M., Timmermans, R.M.A., Roemer, M., Boersen, G.A.C., Builtjes, P., Sauter, F., Velders, G., Beck, J., 2008. The LOTOS-EUROS model: description, validation and latest developments. Int. J. Environ. Pollut. 32, 270–290. doi:10.1504/IJEP.2008.017106

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of Emissions from Air Pollution Sources. 5. C 1 −C 32 Organic Compounds from Gasoline-Powered Motor Vehicles. Environ. Sci. Technol. 36, 1169–1180. doi:10.1021/es0108077

Schell, B., 1996. Zu den Rand- und Anfangswertbedingungen des EURAD Chemie- Transport-Modells Version2 (CTM2): Erstellung eines Szenarios auf der Basis von Messdaten. University of Cologne.

Schell, B., Ackermann, I.J., Hass, H., Binkowski, F.S., Ebel, A., 2001. Modeling the formation of secondary organic aerosol within a comprehensive air quality model system. J. Geophys. Res. 106, 28275–28293.

Schlünzen, H., Sokhi, R.S., 2008. Overview of Tools and Methods for Meteorological and Air Pollution Mesoscale Model Evaluation and User Training. Joint Report of COST Action 728 (Enhancing Mesoscale Meteorological Modelling Capabilities for Air Pollution and Dispersion Applications) and GURME (GAW Urban Research Meteorology and Environment Project).

Schmidt, H., Derognat, C., Vautard, R., Beekmann, M., 2001. A comparison of simulated and observed ozone mixing ratios for the summer of 1998 in Western Europe. Atmos. Environ. 35, 6277–6297. doi:10.1016/S1352-2310(01)00451-4

Senthil Kumar, M., Ramesh, A., Nagalingam, B., 2003. An experimental comparison of methods to use methanol and Jatropha oil in a compression ignition engine. Biomass and Bioenergy. doi:10.1016/S0961-9534(03)00018-7

Serrano, L., Carreira, L., Câmara, R., Gameiro da Silva, M., 2011. On-road performance comparison between two cars consuming petrodiesel and biodiesel, in: 4th International Congress on Energy and Environment Engineering and Management. Merida, Spain, p. 6.

Shao, L.-M., Fan, S.-S., Zhang, H., Yao, Q.-S., He, P.-J., 2013. SO2 and NOx emissions from sludge combustion in a CO2/O2 atmosphere. Fuel 109, 178–183. doi:10.1016/j.fuel.2013.01.027

Sicardi, V., Ortiz, J., Rincón, A., Jorba, O., Pay, M.T., Gassó, S., Baldasano, J.M., 2011. Ground-level ozone concentration over Spain: an application of Kalman Filter post-processing to reduce model uncertainties. Geosci. Model Dev. Discuss. 4, 343–384. doi:10.5194/gmdd-4-343-2011

Singh, A., Smyth, B.M., Murphy, J.D., 2010a. A biofuel strategy for Ireland with an emphasis on production of biomethane and minimization of land-take. Renew. Sustain. Energy Rev. 14, 277–288. doi:http://dx.doi.org/10.1016/j.rser.2009.07.004

Singh, A., Pant, D., Korres, N.E., Nizami, A.-S., Prasad, S., Murphy, J.D., 2010b. Key issues in life cycle assessment of ethanol production from lignocellulosic biomass: Challenges and perspectives. Bioresour. Technol. 101, 5003–5012. doi:http://dx.doi.org/10.1016/j.biortech.2009.11.062

Skamarock, W.C., Klemp, J.B., Dudhia, J., Gill, D.O., Barker, D.M., Huang, X.Y., Wang, W., Powers, J.G., 2008. A Description of the Advanced Research WRF Version 3.

Song, J.-T., Zhang, C.-H., 2008a. An experimental study on the performance and exhaust emissions of a diesel engine fuelled with soybean oil methyl ester. Proc. Inst. Mech. Eng. Part D J. Automob. Eng. 222 , 2487–2496. doi:10.1243/09544070JAUTO932

Song, J.-T., Zhang, C.-H., 2008b. An experimental study on the performance and exhaust emissions of a diesel engine fuelled with soybean oil methyl ester. Proc. Inst. Mech. Eng. Part D J. Automob. Eng. 222 , 2487–2496. doi:10.1243/09544070JAUTO932

Stull, R.B., 1988. An Introduction to Boundary Layer Meteorology, Book. doi:10.1007/978-94-009-3027-8

Sun, J., Caton, J.A., Jacobs, T.J., 2010. Oxides of nitrogen emissions from biodiesel-fuelled diesel engines. Prog. Energy Combust. Sci. doi:10.1016/j.pecs.2010.02.004

Takada, K., Yoshimura, F., Ohga, Y., Kusaka, J., Al., E., 2003. Experimental Study on Unregulated Emission Characteristics of Turbocharged DI Diesel Engine with Common Rail Fuel Injection System. SAE Tech. Pap. 2003-01-31.

Tan, P., Hu, Z., Lou, D., Li, Z., 2012. Exhaust emissions from a light-duty diesel engine with Jatropha biodiesel fuel. Energy. doi:10.1016/j.energy.2012.01.002

Taylor, G., 2008. Biofuels and the biorefinery concept. Energy Policy 36, 4406–4409. doi:http://dx.doi.org/10.1016/j.enpol.2008.09.069

Tchepel, O., 2003. Emission Modelling as a Decision Support Tool for Air Quality Management (Ph.D Thesis). University of Aveiro.

Tchepel, O., Borrego, C., 2010. Frequency analysis of air quality time series for traffic related pollutants. J. Environ. Monit. 12, 544–550. doi:10.1039/B913797A

Tchepel, O., Dias, D., Ferreira, J., Tavares, R., Isabel Miranda, A., Borrego, C., 2012. Emission modelling of hazardous air pollutants from road transport at urban scale. Transport 27, 299–306. doi:10.3846/16484142.2012.720277

Tente, H., Gomes, P., Ferreira, F., Amorim, J.H., Cascão, P., Miranda, A.I., Nogueira, L., Sousa, S., 2011. Evaluating the efficiency of Diesel Particulate Filters in high-duty vehicles: Field operational testing in Portugal. Atmos. Environ. 45, 2623–2629. doi:10.1016/j.atmosenv.2011.02.069

Tesche, T.W., Morris, R., Tonnesen, G., McNally, D., Boylan, J., Brewer, P., 2006. CMAQ/CAMx annual 2002 performance evaluation over the eastern US. Atmos. Environ. 40, 4906–4919. doi:http://dx.doi.org/10.1016/j.atmosenv.2005.08.046

Thunis, P., Georgieva, E., Pederzoli, A., 2012. A tool to evaluate air quality model performances in regulatory applications. Environ. Model. Softw. 38, 220–230. doi:10.1016/j.envsoft.2012.06.005

Tsolakis, A., Megaritis, A., Wyszynski, M.L., Theinnoi, K., 2007. Engine performance and emissions of a diesel engine operating on diesel-RME (rapeseed methyl ester) blends with EGR (exhaust gas recirculation). Energy 32, 2072–2080. doi:10.1016/j.energy.2007.05.016

Turrio-Baldassarri, L., Battistelli, C.L., Conti, L., Crebelli, R., De Berardis, B., Iamiceli, A.L., Gambino, M., Iannaccone, S., 2004. Emission comparison of urban bus engine fueled with diesel oil and “biodiesel” blend. Sci. Total Environ. 327, 147–162. doi:10.1016/j.scitotenv.2003.10.033

Utlu, Z., Koçak, M.S., 2008. The effect of biodiesel fuel obtained from waste frying oil on direct injection diesel engine performance and exhaust emissions. Renew. Energy. doi:10.1016/j.renene.2007.10.006

Van Loon, M., Vautard, R., Schaap, M., Bergström, R., Bessagnet, B., Brandt, J., Builtjes, P.J.H., Christensen, J.H., Cuvelier, C., Graff, A., Jonson, J.E., Krol, M., Langner, J., Roberts, P., Rouil, L., Stern, R., Tarrasón, L., Thunis, P., Vignati, E., White, L., Wind, P., 2007. Evaluation of long-term ozone simulations from seven regional air quality models and their ensemble. Atmos. Environ. doi:10.1016/j.atmosenv.2006.10.073

Vautard, R., Schaap, M., Bergström, R., Bessagnet, B., Brandt, J., Builtjes, P.J.H., Christensen, J.H., Cuvelier, C., Foltescu, V., Graff, A., Kerschbaumer, A., Krol, M., Roberts, P., Rouïl, L., Stern, R., Tarrason, L., Thunis, P., Vignati, E., Wind, P., 2009. Skill and uncertainty of a regional air quality model ensemble. Atmos. Environ. doi:10.1016/j.atmosenv.2008.09.083

Verwer, J.G., Spee, E.J., Blom, J.G., Hundsdorfer, W., 1999. A second-order Rosenbrock method applied to photochemical dispersion problems. SIAM J. Sci. Comput. 20, 1456–1480. doi:10.1137/S1064827597326651

Walcek, C.J., Taylor, G.R., 1986. A Theoretical Method for Computing Vertical Distributions of Acidity and Sulfate Production within Cumulus Clouds. J. Atmos. Sci. 43, 339–355. doi:http://dx.doi.org/10.1175/1520-0469(1986)043<0339:ATMFCV>2.0.CO;2

Wang, W., Bruyère, C., Duda, D., Dudhia, J., Gill, D., Kavulich, M., Keene, K., Chuan, H.-C., Michalakes, J., Rizvi, S., Zhang, X., 2014. WRF-ARW Version 3 Modeling system user'd guide.

WHO - World Health Organization, 2014. 7 million premature deaths annually linked to air pollution. News release, 25th March.

Wilczak, J., McKeen, S., Djalalova, I., Grell, G., Peckham, S., Gong, W., Bouchet, V., Moffet, R., McHenry, J., McQueen, J., Lee, P., Tang, Y., Carmichael, G.R., 2006. Bias-corrected ensemble and probabilistic forecasts of surface ozone over eastern North America during the summer of 2004. J. Geophys. Res. doi:10.1029/2006JD007598

Wu, F., Wang, J., Chen, W., Shuai, S., 2009. A study on emission performance of a diesel engine fueled with five typical methyl ester biodiesels. Atmos. Environ. 43, 1481–1485. doi:10.1016/j.atmosenv.2008.12.007

Wyatt, V.T., Hess, M.A., Dunn, R.O., Foglia, T.A., Haas, M.J., Marmer, W.N., 2005. Fuel properties and nitrogen oxide emission levels of biodiesel produced from animal fats. J. Am. Oil Chem. Soc. doi:10.1007/s11746-005-1113-2

Xue, J., Grift, T.E., Hansen, A.C., 2011. Effect of biodiesel on engine performances and emissions. Renew. Sustain. Energy Rev. 15, 1098–1116. doi:http://dx.doi.org/10.1016/j.rser.2010.11.016

Zhang, L., Brook, J.R., Vet, R., 2003. A revised parameterization for gaseous dry deposition in air-quality models. Atmos. Chem. Phys. 3, 2067–2082. doi:10.5194/acp-3-2067-2003

Zhao, R., Bean, S.R., Wang, D., Park, S.H., Schober, T.J., Wilson, J.D., 2009. Small-scale mashing procedure for predicting ethanol yield of sorghum grain. J. Cereal Sci. 49, 230–238. doi:http://dx.doi.org/10.1016/j.jcs.2008.10.006

Zhu, L., Zhang, W., Liu, W., Huang, Z., 2010. Experimental study on particulate and NOx emissions of a diesel engine fueled with ultra low sulfur diesel, RME-diesel blends and PME-diesel blends. Sci. Total Environ. 408, 1050–8. doi:10.1016/j.scitotenv.2009.10.056

List of web pages consulted

URL 1 – General Motors (http://www.gm.com/vision/greener_vehicles.html)

URL 2 – Shell Global (http://www.shell.com/global/environment-society/environment/climate-change/biofuels-alternat)

URL 3 – DGEG – Direcção Geral de Energia e Geologia (http://www.dgeg.pt/)

URL 4 – EBB – European Biodiesel Board (http://www.ebb-eu.org/)

URL 5 – EIA – US Energy Information Administration (http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm)

URL 6 – APPB – Associação Portuguesa de Produtores de Biocombustiveis (http://appb.pt/)

URL 7 – IFAP – Instituto de Financiamento da Agricultura e das Pescas (http://www.ifap.min-agricultura.pt/)

URL 8 – LNEG – Laboratório Nacional de Energia e Geologia (http://www.lneg.pt/)

URL 9 – INE – Instituto Nacional de Estatística (http://www.ine.pt/)

URL 10 – PORDATA – Base de dados de Portugal contemporâneo (http://www.pordata.pt/Municipios/Venda+de+combustiveis+para+consumo-34)

URL 11 – FAIRMODE – Forum for AIR quality MODelling in Europe (http://fairmode.jrc.ec.europa.eu/)